DYNATECH R/D COMPANY

DIRECT LIQUEFACTION OF PEAT AND LIGNITE TO BTX-TYPE LIQUID FUEL

Final Technical Report for Period:
June 1, 1981 - August 31, 1984

DOE Contract No. DE-AC01-81ER10914-2
Dynatech Project No. DOE-6
Dynatech Report No. 2314

Submitted to:

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October 26, 1984

a division of DYNATECH CORPORATION

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SUMMARY

This report relates the work on the experimental research and development program for the direct liquefaction of peat and lignite to a BTX-type liquid fuel. This work was carried out in the final year of a three-year Department of Energy (Advanced Energy Projects Division) sponsored program. The liquefaction study built on the experimental work done in the first two years of the program which was directed towards the development of a biochemical process for production of alcohol fuel from peat.

Both the BTX-type and alcohol fuel processes have as their major feature an alkaline hydrolysis pretreatment of the peat and lignite. The goal of this pretreatment is the breakdown of the complex macromolecular peat and lignite structures to simple aliphatic and aromatic compounds. Owing to the geological history of the peat and lignite, these organic compounds are highly oxygenated and, under alkaline conditions, water-soluble to a large extent. It was proposed to investigate the susceptibility of these organics to further chemical treatment and biological treatment for production of BTX-type and alcohol fuels, respectively.

The work directed toward the production of BTX-type fuel was done this past year and is detailed in this report. The experimental program involved laboratory scale work in two process steps:

(1) alkaline hydrolysis for pretreatment; and

(2) catalytic decarboxylation for conversion of pretreatment products to BTX-type fuel.

Both of these areas were approached independently to establish the technical feasibility of the operation and to determine process operating conditions and yields.

The pretreatment experiments called for reaction of lignite, water, and sodium carbonate under batch conditions. The optimal conditions

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for breakdown of the lignite were found to be 250°C (ϕ hours, 8% volatile solids loading, and 20% sodium carbonate (weight by weight volatile solids)). Under these conditions, 63% of the input lignite volatile solids were solubilized. Longer reaction times and/or higher temperatures resulted in repolymerization, i.e., further coalification, of the hydrolysis products. A decrease in alkali or an increase in solids loading resulted in lower yields. This work is presented in Section 3.

Decarboxylation experiments were carried out using benzoic acid and pretreated lignite. Two procedures for chemical decarboxylation were investigated:

(1) the copper/quinoline method; and

(2) the persulfate/silver ion method.

The former method showed some conversion of benzoic acid to benzene, but quantitation was difficult with the complexity of the product mixture. The latter method showed an identifiable 41% yield of benzene. Because the persulfate/silver ion decarboxylation is carried out in an aqueous medium, it was the preferred method for lignite decarboxylations. Under conditions analogous to the model studies using persulfate/silver, lignite hydrolysate was subjected to decarboxylation. The product mixture showed 6% conversion of the hydrolysate to volatile organic liquid, i.e., 4% overall conversion of the input lignite volatile solids. The decarboxylation work is detailed in Section 4.

The preliminary engineering designs for pilot and full-scale facilities are presented in Sections 5 and 6, respectively. The pilot-scale facility is actually an expanded scale laboratory facility which accommodates both CSTR and plug flow reactors. The facility is designed for the extraction of the necessary engineering data, specifically detailed time/temperature profiles. The lack of this capability was found to be a limiting factor in the batch reactor work using lignite.

The capital and operating costs for a full-scale facility are also detailed within. This analysis utilized the Aspen Plus® computer model in the calculation of all material flows, process energy requirements, equipment sizing, and equipment characterizations. The costing was for the "base case" process where 63% of the input lignite volatile solids are solubilized and 50% of the solubilized material is decarboxylated. For a 20,000 TPD plant producing an 18,000 BTU/lb liquid fuel, the fuel cost is $1.16 per gallon. This price is most sensitive to solids loadings in the pretreatment reactor. The complete design, costing, and sensitivity analysis is detailed in Section 6.

Section 1

INTRODUCTION

1.1 The Focus on Peat and Lignite

The diminishing world-wide petroleum reserves and rising crude oil prices have created the need to find other raw materials for the production of fuels and feedstock chemicals. Private industry and the state and federal governments are undertaking a substantial research and development program to utilize other readily available resources to bridge the gap between supply and demand. The sizeable deposits of peat and lignite in the United States may provide raw materials for the production of significant quantities of liquid fuels and organic chemicals as well as fuel gas.

With the exception of this DoE-AEPD sponsored project, the DOE focus on peat utilization has been largely directed to producing pipeline quality methane from peat. In a similar manner, lignite utilization has been directed largely to producing substitute natural gas — an example being the Great Plains Gasification Plant in Beulah, North Dakota. The great potential for both peat and lignite is to be realized only if a full range of fuels, not just substitute gas, is produced from peat and lignite.

The energy resources associated with peat and lignite are as follows:

PEAT: Recent estimates indicate that peat covers approximately 152 x 10^6 hectares (375 million acres) of the earth's surface. Sufficient quantities of peat reserves exist in the United States to make this a potentially valuable natural resource. A comparison with other energy reserves shows that peat reserves (1,443 quads) are greater than the energy from uranium (1,156

quads), shale oil reserves (1,160 quads), and the combined reserves of petroleum and natural gas (1,408 quads) (Rader 1977). Only coal reserves (5,000-10,000 quads) represent a greater energy reserve in the U.S. The quantity of peat makes it a vast and largely untapped potential energy source, an alternative to imported petroleum.

LIGNITE: In addition to peat, the use of selected lower rank coals, especially lignite, should be considered for processing. In this regard, it is of interest to consider the amount and location of lignite in the United States. A breakdown of all the estimated coal reserves in the United States for the four major ranks of coals is given as follows (Aueritt 1967):

Coal Rank	Remaining Recoverable Reserves (billion tons)	Percent of Total
Bituminous	671	43.0
Sub-bituminous	428	27.4
Lignite	447	28.7
Anthracite	13	0.9
	1,559	100.0

If only sub-bituminous coal and lignite are considered as especially suitable to the proposed process, then it is seen that this amounts to 56.1% of remaining recoverable coal reserves.

The location of peat and lignite reserves in the United States is of interest. It is seen that lignite is located largely in Montana, Wyoming and North Dakota. Peat is located largely in Minnesota, Michigan, and North Carolina. It is interesting to consider the regional impact of the processes utilizing peat and lignite with respect to current coal production. The present leading coal producing states are, in decreasing order of production, West Virginia, Kentucky, Pennsylvania, Illinois, Ohio,

and Virginia (1968 production figures [National Coal Association 1974]). These states are those with substantial reserves of bituminous coal. Thus, the development of a process for conversion of peat and lignite would have a substantial national impact, because such conversion will take place in areas where coal is not presently mined. Thus, the use of an environmentally acceptable technique would be acceptable.

1.2 Peat and Lignite Utilization

The combustion of either dry peat or lignite will release the greatest amount of energy (approximately 10,000 BTU/lb). However, because peat is harvested from bogs, its moisture content is high, and combustion requires pre-drying, a costly and energy-intensive process. In a similar manner, lignite has both a high moisture content and a high ash content. Conventional combustion for electrical power — when applied to either peat or lignite — has been found economically unattractive.

The problems associated with combustion of low-rank coals can be avoided by taking advantage of alternative utilization methods. The peat and lignite can be used as fuels in several forms. Solid fuel utilization methods traditionally rely on methods for carbonizing, briquetting, or drying. Additional methods for solids beneficiation, such as desulfurization, require some physical or chemical pretreatment. Gasification of low-rank coals is another utilization method, but one which will require some eventual process adaptation for special applications to high moisture, high ash coals. Liquefaction is also a probable technology for utilization of low-rank coals. Here, also, the technology of the major bituminous coal liquefaction processes must be adapted and improved if the methods are to meet with reasonable success using peat and lignite.

As an alternative, it was proposed to wet process peat and lignite and convert these materials to liquid and gaseous fuels. Specifically, the objective of this work has been recovery of the energy from peat and lignite in the form of both liquid and gaseous fuels. For

each case, the conversion process is carried out in two stages. In the first stage, the coalified material, i.e., the peat or lignite, undergoes hydrolysis to reduce the complex aromatic molecular structure to simple aromatics. In the second stage of the process, the simple aromatics are either anaerobically fermented to fuel gas or otherwise converted to liquid fuel, such as pentanol or benzene. Thus, the conversion process applied to the coalified materials is a combination of an initial hydrolytic treatment ("pretreatment") and a chemical or biological treatment. Biological treatment of peat hydrolysates for production of chemicals was investigated in the first two years of this program (Dynatech Report No. 2260, Levy et al., 1983). Chemical treatment of lignite hydrolysates was the focus of the third year of this program and will be detailed here.

Section 2

PROGRAM PLAN

2.1 Overview of the Program Plan

The entire program was carried out over a three-year period. The first two years of the program focused on the process for the conversion of peat to an alcohol fuel. The laboratory plan for this work was divided into three stages: (1) alkaline oxidation of peat, (2) microbial conversion of solubilized peat to organic acids, and (3) electrolytic oxidation of the organic acids to alcohol fuels. The laboratory work identified optimal loading rates, temperatures, residence times, etc., for each stage of the process. These experimental results provided the bases for the engineering design and economic analyses for a full-scale facility, and preliminary design of a pilot-scale facility for the conversion of peat to an alcohol fuel. The full account of this work was presented in a previous report (Dynatech Report No. 2260, Levy et al., 1983).

Having identified an appropriate experimental method for the hydrolytic breakdown of the peat, work was directed toward applying similar reaction chemistry to lignite. The emphasis was on coordinating alkaline hydrolysis and chemical decarboxylation with the goal of producing a BTX-type liquid fuel from lignite. The intention of this program was to examine the operating parameters of the proposed stages: (1) alkaline hydrolysis of lignite, (2) oxidation of hydrolysis products, and (3) decarboxylation of the final hydrolysate to BTX-type liquid fuel. Those results led to preliminary engineering designs for full and pilot-scale facilities.

2.2 The Program Outline

The lignite liquefaction program to produce a BTX-type liquid fuel included work on pretreatment of lignite, recovery of pretreated lignite material, and subsequent conversion of the lignite products to

BTX-type liquid fuel. Included in this program was a preliminary engineering economic analysis for full and pilot-scale facilities to project process costs. The work described herein was to conduct the experimental process development work for the proposed lignite liquefaction process. A complete description of the program tasks specific to this last year follows.

Task 1: Pretreatment of Lignite to Form Water-Soluble Aromatics

Alkaline pretreatment of peat under oxidative conditions (up to 200°C) promotes degradation of the peat and lignite to low molecular weight, water-soluble aromatics suitable for anaerobic fermentation. Somewhat more severe pretreatment conditions of lignite (up to 300°C) were employed to attain optimum solubilization and conversion to simple aromatics suitable for a liquid fuel. Parameters investigated included pH, temperature, solids loading, oxygen concentration, and time. This liquefaction study was built on the peat work which was oriented toward the goal of pretreatment with fermentation to chemicals. The principal objective of this task was to maximize conditions for yield of soluble material from lignite.

Task 2: Decarboxylation of Water Soluble Aromatics

The alkaline hydrolysis of lignite was to yield water soluble aromatics for recovery as a liquid fuel. This concept was built on the results of the earlier work where this treatment technique was used to break the complex lignin-like, aromatic structure of peat for fermentation. An example of the type of product which was anticipated is benzoic acid. This single-ring aromatic is a benzene ring with one carboxylic acid group capable of salt formation and, thus, water-soluble functionality. Upon further treatment at slightly higher temperatures, the benzoic acid will undergo decarboxylation to yield benzene, a possible liquid fuel. In a similar manner, other single ring carboxylic acids would, upon decarboxylation, yield BTX-type liquid fuels. This was the basis of the liquid fuel recovery technique investigated as part of this program task. The objective of this task was to establish the conditions for the conversion of the water soluble lignite aromatics to BTX-type liquid fuel.

Task 3: Chemical Analysis for Documentation and Verification of Results

Integral to the overall program was the chemical analysis. Methods used in the evaluation of lignite included gel permeation chromatography (GPC), high pressure liquid chromatography (HPLC), gas chromatography (GC) and standard wet chemistry and gravimetric extraction procedures. In addition, viscosities were run using model BTX-type liquid fuels to verify suitability as a liquid fuel and to establish a basis for comparing this material to petroleum-based liquid fuels.

Task 4: Evaluation of Product Recovery Systems

A system was designed for removal and recovery of the BTX-type fuel.

Task 5: Preliminary Process Economics for a Pilot and Full-Scale Facility

This task provides estimates of the capital and operating costs for a pilot and a full-sized facility based on data obtained from the experimental program. Additional research requirements were also delineated. A computer-aided optimization and sensitivity analysis was also performed to determine desired plant operating conditions. Preliminary conceptual designs for adaption of this process to an integrated energy recovery system were prepared and cost estimates made for the BTX-type fuel facility.

Task 6: Industrial/University Review Committee and Workshop

An Industrial/University Review Committee was instated to facilitate the transfer of DoE-sponsored technology to industry and to provide for practical direction to meet industry needs. To this end, the review committee included industrial participation from those firms: a) controlling peat and lignite natural resources; b) involved in converting fossil fuels to marketable motor fuel products; c) conducting engine testing; d) carrying out environmental assessment of alternative fuels; and

e) employing process development engineers. Providing further balance to the industrial participants were several participants from universities. Regular meetings of the Review Committee were held (see Appendix C.)

2.3 Program Outline: Objectives and Accomplishments

Task 1: Pretreatment of Lignite to Form Water-soluble Aromatics

OBJECTIVE: Determine conditions of maximum solubilization

ACCOMPLISHMENTS:

- Established conditions for maximum solubilization of lignite.
- Investigated effect of percent solids loading on solubilization.
- Determined effect of oxygen flow rate on solubilization.

Task 2: Decarboxylation of Water-soluble Aromatics

OBJECTIVE: Establish conditions for conversion of water-soluble aromatics to BTX-type liquids.

ACCOMPLISHMENTS:

- Achieved decarboxylation of model compounds, to yield BTX-type liquids.
- Investigated decarboxylation of treated lignite.

Task 3: Chemical Analysis for Documentation and Verification of Results

OBJECTIVE: Establish appropriate analytical scheme.

ACCOMPLISHMENTS:

- Employed standard wet chemical and gravimetric techniques as well as colorimetry and viscometry to characterize starting material and products.

- Utilized gel permeation chromatography, thin layer chromatography, high pressure liquid chromatography and gas chromatography to analyze products.

Task 4: Evaluation of Product Recovery Systems

OBJECTIVE: Design system for removal and recovery of BTX.

ACCOMPLISHMENTS:

- Investigated product recovery systems.

Task 5: Preliminary Process Design for a Pilot and Full-scale Facility

OBJECTIVES: - Establish preliminary conceptual designs.
- Estimate capital and operating costs.
- Delineate additional research requirements.

ACCOMPLISHMENTS:

- Established preliminary design.

- Determined major equipment costs for pilot facility.

- Determined capital and operating costs for full-scale facility.

- Defined additional research requirements.

Task 6: Industrial/University Review Committee Meetings and Review

OBJECTIVE: Provide practical direction via review and comment.

ACCOMPLISHMENTS:

- Held periodic committee meetings
- Conducted a workshop to review project results.

Task 7: Technical Reporting

OBJECTIVE: Prepare comprehensive technical reports.

ACCOMPLISHMENTS:

- Provided interim progress reports.
- Prepared comprehensive technical report at conclusion of project.

Section 3

ALKALINE SOLUBILIZATION AND OXIDATION OF LIGNITE

3.1 Background

3.1.1 The Origins of Lignite

A combination of chemical, biological and physical processes contributes to the natural decomposition of plant material. The various plant constituents decompose at different rates in accordance with their respective susceptibilities to these natural mechanisms of attack. Thus, over time, the deposition of plant materials represents an accumulation of differentiated responses to different geological phenomena.

The plant constituents are accumulated as peat, a material which is composed primarily of macerals, less so of minerals, with water and gases in pore-like interstices. The macerals represent the organic constituents of the plant material, e.g., cellulose and lignin. As all of these materials are variably subjected to decay, they are incorporated into sedimentary strata, and altered by natural physical and chemical processes. As the material is acted upon, it undergoes a molecular metamorphosis manifested in the generation of "new" materials which are physically distinct and unique in their fundamental properties. This process is known as "coalification."

3.1.2 The Structure of Lignite

As peat is subjected to geological alteration, its organic constituents become chemically more complex. The severity of the conditions affects the physical properties of the resultant material. This coalified material is then classified according to rank with the lignites at the low-rank, followed by sub-bituminous, bituminous, and anthracitic coals.

Because lignite is in the early stages of coalification, it retains some of the characteristics of wood. Pieces of plant debris and remains of cellular structure are visible in electron micrographs. The

molecular structure then represents the earliest stages of geological metamorphism of plant material.

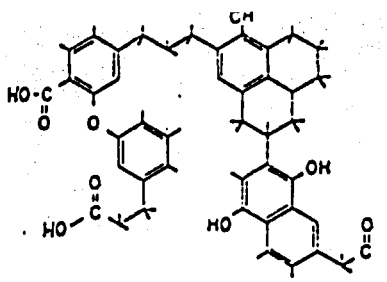
The major structural constituents of lignite are derived from three sources: a) cellulose; b) lignin; and c) other plant components, e.g., protein, dispersed in the plant tissues. The coalification process is a deoxygenation/dehydration process. In the early stages, coalification does not create a large number of tertiary bonds. Because these are the bonds which contribute to a strong three-dimensional structure, lignites have loose structures.

The molecular structure of the organic portion of lignite can be represented as shown in Figure 3.1. The major features are summarized as follows. First, in comparison to higher rank coals, lignites have low aromaticity. Lignite is approximately 60% aromatic, peat 50%, and bituminous greater than 70%. Second, aromatic clusters are primarily one and two rings, i.e., aromatics have not yet fused into complex multi-ring forms. In contrast, bituminous coals are comprised of fused ring systems of 3 or more aromatics. Finally, oxygen-containing functional groups are prevalent. These groups are represented by carboxylate, phenolic and ethereal components, groups which chemically account for the complex fused-ring structure of higher rank coals.

The remaining lignite components are moisture and ash. Again, the relative proportions of these are indicative of the rank of lignite. Lignite typically has a high moisture content when compared to other (higher rank) coals. Water is incorporated into the lignite matrix in an intermolecular hydrogen bonding between the water and the oxygen functional groups in the lignite. The ash-containing portion of lignite can be further divided into the inorganics and the minerals. The inorganics, e.g., calcium and sodium, are to some extent relatively mobile ions, presumably associated with the carboxylic acid functional groups; thus, some lignites can have levels of these inorganics. The mineral matter is primarily represented by clays, pyrite, and quartz. Frequently, the mineral particles are quite small and often appear finely dispersed throughout the carbonaceous material.

Figure 3.1

Structural Features of Lignite



Adapted with modification from Sondreal et al., 1982.

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3.1.3 The Reactivity of Lignite

Examination of the organic portion of the lignite matrix as represented in Figure 3.1 reveals several important clues to its potential reactivity. A large portion of the aromatic material exists as single rings. These aromatics are joined in a network of carbon-carbon and carbon-oxygen linkages. Aliphatic units are incorporated as aromatic side-chains, alone or in conjunction with other aromatic groups.

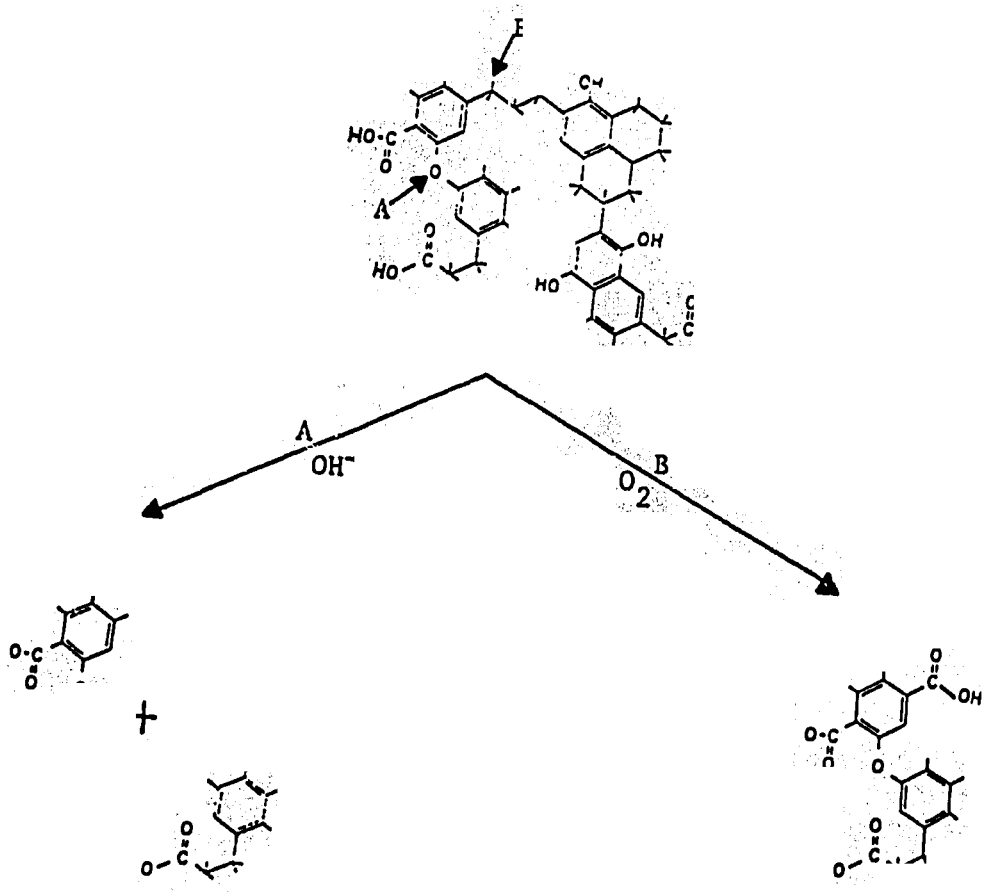
This matrix structure is representative of a particular stage of the coalification process, a continuous process of deoxygenation which has resulted in the structural elimination of water. It is this process which contributes to the increasing molecular complexity up through the coal ranks. Thus, it might be expected that reversal of the coalification by hydrolytic reaction could result in considerable degradation of the coal structure into simpler units. This is true especially in the lower ranks of coals, e.g., peat and lignite.

Alkaline hydrolysis can be exploited in conjunction with oxidative processes to break certain well-defined bonds in the lignite. The carbon-oxygen linkages are particularly susceptible to the alkaline hydrolysis. Likening the lignite structure to a polyester/polyether-type material, phenols and carboxylic acids will be the probable products of a base hydrolysis (Figure 3.2a). The carbon-carbon linkages, as found, for example, in the alkylbenzene portions of the lignite matrix, can be effectively cleaved upon oxidation. Generally, the products of an oxidation will be carboxylic acids (Figure 3.2b). Thus, a careful "aqueous alkali oxidation" can effect a reversal of the coalification process particularly in low rank coals.

The effectiveness of an aqueous alkali oxidation will be primarily dependent upon the structural "maturity" of the organic matrix and not upon the ash or moisture characteristics of a ranked coal. A treatment process which incorporates the elements of an alkaline hydrolysis will obviously require water and alkali. Lignites obtained from different

Figure 3.2

Aqueous Alkali Oxidation of Lignite



A Alkaline hydrolysis
B Oxidation

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sources vary primarily in ash and moisture content; the organic matrices are similar. Thus, the degree of lignite reactivity, as judged by breakdown potential, can theoretically be regulated by adjustment of added water and alkali in consideration of inherent moisture and ash for a particular sample.

3.2 Program Plan for Alkaline Solubilization and Oxidation of Lignite

The objective of the solubilization and oxidation of lignite is the production of single-ring aromatic compounds which can be treated to yield BTX-type liquids. Solubilization of lignite has been accomplished under alkaline conditions. Based on Dynatech's previous work with peat, it was suggested that oxidation would increase the yield of low-molecular weight products.

With these objectives in mind, the following program plan was proposed:

- Characterization of raw lignite;
- Investigation of varying solubilization conditions (e.g., solids loading, temperature, concentration of alkali, type of alkali);
- Investigation of varying oxidation conditions (e.g., flow rate of input circulation);
- Characterization of products using standard wet chemical techniques and analytical instrumentation (e.g., extraction, gravimetric analysis, HPLC, GC, GPC, IR, spectroscopy, petrography);
- Evaluations and optimization of experimental procedures;
- Isolation of BTX-type products; and
- Preparation of an appropriate process design.

3.3 Alkaline Solubilization and Oxidation of Lignite — Experimental Procedures

3.3.1 Determination of Lignite Characteristics

Before investigating solubilization and oxidation procedures it was necessary to determine various characteristics of the lignite. Two samples of lignite were received from Meridian Land and Mineral Company (Billings, Montana). These samples were labelled "Buelah" and "Gascoyne," indicating the origin of the lignite. The Buelah lignite was used for this study.

First, the Buelah lignite was sent to Resource Engineering Incorporated (REI) of Waltham, Massachusetts, to be crushed. After being crushed to ¼-inch, a sample of the material was retained by REI for ultimate and proximate analysis (report in Appendix A). The remainder of the crushed lignite was wet-packed and returned to Dynatech.

The final type of analysis performed on the untreated lignite was the solids analysis done on the stock lignite slurry and the pre-treatment slurries. The stock lignite slurry was prepared by wet ball milling the ¼-inch wet-packed crushed lignite (as received from REI) and sieving to -100 mesh. Pre-treatment slurry was prepared by diluting the stock slurry to the required percent volatile solids, then adding the appropriate amount of alkali.

Two types of solids analysis were performed: (1) total solids, and (2) ash content. Total solids were determined by the following method. Samples were measured into dry round-bottom flasks and the volume reduced *in vacuo* using a Buchi Rotavapor-R rotary evaporator. The flasks were then placed in a desiccator over anhydrous $CaSO_4$ and dried *in vacuo* to constant weight.

After drying, the ash content was determined. Samples were measured into dry evaporating dishes and placed in a 100°C Blue M Stabil-Therm

Gravity Oven for six hours. The samples were then cooled and weighed. The dried samples were heated at 600°C in a Lindberg M51442 muffle furnace for six hours. After cooling in a desiccator, the residual material was weighed to determine ash content. Volatile solids were determined from the difference between the total solids and the ash.

3.3.2 Preparation of the Lignite Slurry

A stock lignite slurry was prepared by wet ball milling the 1/4-inch wet-packed crushed lignite sample (as received from REI) and sifting to -100 mesh. Pre-treatment slurry was prepared by diluting the stock slurry to the required percent volatile solids, then adding the appropriate amount of alkali on the basis of grams carbonate per gram of lignite volatile solids.

3.3.3 Solubilization Experiments

Solubilization parameters were extensively investigated to determine optional reaction conditions. The factors investigated were:

- Temperature
- Time
- Amount of alkali
- Type of alkali
- Loading of volatile solids.

A. Time/Temperature

A series of treatments was conducted at different temperatures. The charge to the reactor was kept constant at 7.5% volatile solids and 0.2 gram Na_2CO_3/gram volatile solids for this study. The three temperatures studied were 200°C, 250°C and 300°C. Samples were taken at designated intervals during the treatment.

B. Amount/Type of Alkali

The second series of experiments was designed to investigate the effects of different types of alkali and of different amounts of alkali.

Two compounds were chosen as alkali: NaOH and Na_2CO_3. A single treatment using NaOH was done at 300°C. The NaOH used was equal in sodium-equivalents to the Na_2CO_3 used in the time/temperature series described previously (i.e., 3.8 sodium meq/gram volatile solids). In addition, the effect of varying the amount of Na_2CO_3 was also investigated. The amount of Na_2CO_3 added was varied from 0.05g Na_2CO_3 to 0.3g Na_2CO_3 per gram volatile solids. Finally, a control treatment, with no additive, was also performed.

C. Solids Loading

The final solubilization factor investigated was the amount of volatile solids used for the treatment. This amount varied from 4.0% to 11.9% volatile solids (w/v) in the slurry charged to the reactor.

3.3.4 Oxidation Experiments

After evaluating factors which directly affect solubilization, the process of oxidation and its effects on the overall solubilization were investigated. A series of experiments was designed to examine the effect of different air flow rates on solubilization of volatile solids. In addition, a set of experiments was conducted to investigate the oxidation of solubilized hydrolysis products compared to non-solubilized hydrolysis products.

The first series of oxidations investigated the effect of the input air flow rate. Three flow rates were chosen; temperature, concentration of Na_2CO_3, and lignite loading were held constant for the three oxidations. The flow rates chosen were 400 mL/min, 740 mL/min and 1000 mL/min. The oxidations were done at 200°C, with 0.5g Na_2CO_3 per gram volatile solids and a 4% VS loading. In all three oxidations, samples were taken at designated intervals for solids analysis.

The second series of oxidations investigated the effects of oxidation on solubilized vs. non-solubilized hydrolysis products. An initial hydrolysis was conducted to provide solubilized and non-solubilized product. This treatment was done at 250°, with 0.25g Na_2CO_3/g VS and an 8% VS

loading. The mixture was brought up to 250°C and then cooled. Solubilized material was separated from non-solubilized material by centrifugation at 8800 x g for 15 minutes. The entire batch of treated material was centrifuged. The supernatant material was designated the "solubilized" and the pellet material was designated the "non-solubilized."

The next step in this set of experiments was oxidation of these two materials. Both oxidations were conducted under the same conditions at 200° C, with 0.5g Na_2Co_3/g VS and a 4% VS loading.

3.3.5 Analytical Methods

Treatment samples were characterized via solids analysis, percent extractables, and petrography. Solubilized material was analyzed via high performance liquid chromatography (HPLC) and gas chromatography (GC), and extracted samples were analyzed for molecular weight distribution via gel permeation chromatography (GPC).

A. Solids Analysis

Reaction samples are measured into dry round bottom flasks. The samples are initially reduced *in vacuo* using a Buchi Rotavapor-R rotary evaporator. The flasks are subsequently placed in a desiccator over anhydrous $CaSO_4$ and dried *in vacuo* to constant weight for determination of total solids.

Another aliquot of the reaction mixture (pellets, supernatants, or slurries) is measured into a dry evaporating dish. For the determination of oven-dried material, the dish is placed in a 100°C Blue M Stabil-Therm Gravity Oven for 6 hours, cooled, and weighed for oven-dried total solids. Subsequently, the dried material is heated at 600°C in a Lindberg M51442 muffle furnace for an additional 6 hours. After cooling, the residual material is weighed for the determination of ash content.

B. Percent Extractables

A pellet, isolated from an acidified portion of reaction slurry, is placed in a beaker and dried to constant weight *in vacuo*. It is stirred with 20 mℓ tetrahydrofuran for one hour, then stirred with warming for five minutes. The mixture is vacuum filtered into a tared beaker and the filtrate is allowed to dry to constant weight to determine percent extractable solids.

C. Petrography

Petrographic analyses were performed by Resource Engineering Incorporated, Waltham, MA (report in Appendix A). Pre- and post-treatment samples were submitted. The pre-treatment sample was obtained from a portion of the lignite as provided. The post-treatment sample was obtained after washing and drying the pellet isolated by centrifugation. (The reaction slurry was first acidified to pH 2 with concentrated HCl.)

D. High Performance Liquid Chromatography

The liquid chromatograph used is a Waters system equipped with a M-45 solvent delivery system, a U6K injector, a free standing model 440 absorbance detector set at 254 nm, and a 10-mv strip chart recorder. The column used was a Regis Octadecyl Workhorse (30 cm x 4.6 mm).

A monocratic eluent system was chosen on the basis of its ability to separate four characteristic products (benzoic acid, syringic acid, syringaldehyde, and vanillin). This system was 45% MeOH/1% H_3PO_4. Spectro-grade glass-distilled methanol is obtained from Burdick and Jackson Laboratories, Inc. Phosphoric acid is Mallinckrodt reagent grade. Distilled water is filtered, deionized, and passed through a carbon bed in a system from Sybron/Barnstead. After the solvent system is prepared, it is filtered through a Millipore type HA 0.45-μm filter and degassed with a Branson sonicator before use.

Solutions of 5-10 μg/mℓ of the standards (benzoic acid, syringic acid, syringaldehyde, and vanillin) are prepared in 45% MeOH. The retention volumes of these standards are determined by injecting 100 μℓ of the solutions into the aforementioned chromatographic system. Filtered reaction solutions are diluted with MeOH and characterized with respect to this standardization.

E. Gas Chromatography

The volatile organic liquid determinations in this phase of the study are made using a Perkin-Elmer gas chromatograph equipped with a Gow-Mac Series 750 flame ionization detector and a Houston Instrument OmniScribe recorder. The separation is carried out on a Chromasorb 101 column (1/4 in. x 5 ft) under conditions of linear programming over the temperature range 100-200°C (15°C/min) with nitrogen as the carrier gas. The chromatograph is calibrated for analysis of methanol, acetone, acetic acid, propionic acid, butyric acid, and valeric acid. Reaction samples are filtered using a Millipore HA filter before injection.

F. Gel Permeation Chromatography

The extracts obtained from the extraction are analyzed by gel permeation chromatography in order to determine the size of the molecules which are extractable. Tetrahydrofuran is used as the carrier solvent. The column is restyragel packed, 30 cm long. A Waters Associates chromatography pump Model 6000A, and Waters Differential Refractometer R401 detector is used.

3.4 Results and Discussion of Solubilization and Oxidation Experiments

The extensive investigation of solubilization parameters and the effects of oxidation reveal several interesting conclusions. These conclusions are discussed in the following sections.

3.4.1 Temperature/Time Studies

Following the experimental protocol established in the first quarter of work, a testing regime was set up in which lignite was heated with aqueous alkali at various temperatures. The goal was to determine the influence of temperature and time on the degree of lignite breakdown under conditions of alkaline hydrolysis. This phase of the experimental program can be summarized as a series of three basic temperature/time experiments: (1) 200°C/4 hrs, (2) 250°C/4 hrs, and (3) 300°C/5.75 hrs. In each experiment, a lignite slurry was treated at the specified temperature with samples being withdrawn when the reactor reached temperature, and 0.5 hour, 1.0 hour, 20 hours, and 4.0 hours (or 5.75 hours) thereafter. Each of these "hot-drawn" samples was characterized with respect to the percent of the input volatile solids solubilized and the percent isolable, THF-extractable material. In the first quarter of work, this analytical format was established as the one which would best accommodate the needs of the program by providing an informative scientific and engineering data base. In addition, the samples were qualitatively evaluated with respect to physical appearance.

3.4.2 Physical Characterization

A. Appearance

The final product slurries of alkaline solubilizations at 200°, 250°, and 300°C compare as follows. The 200°C product is gelatinous (mud-like) and does not settle over time. It is medium brown in color, and does not disperse at all, or generate any surface film when dropped into clean water. By contrast, the 250°C product is a mobile, yellowish brown liquid of high opacity; when dropped into water is rapidly generates a small, stable surface film. The 300°C product is an oily slightly brownish grey/black mobile liquid of somewhat stronger odor than the others, when dropped into water is generates a very rapidly spreading surface film, which subsequently contracts and wrinkles. Both the 250°C and the 300°C products

throw dense layers of solid upon standing; however, in all cases the particulate nature of the products, though not directly visible, is demonstrated by a slow diffusion speed in water.

B. Scanning Electron Microscopy

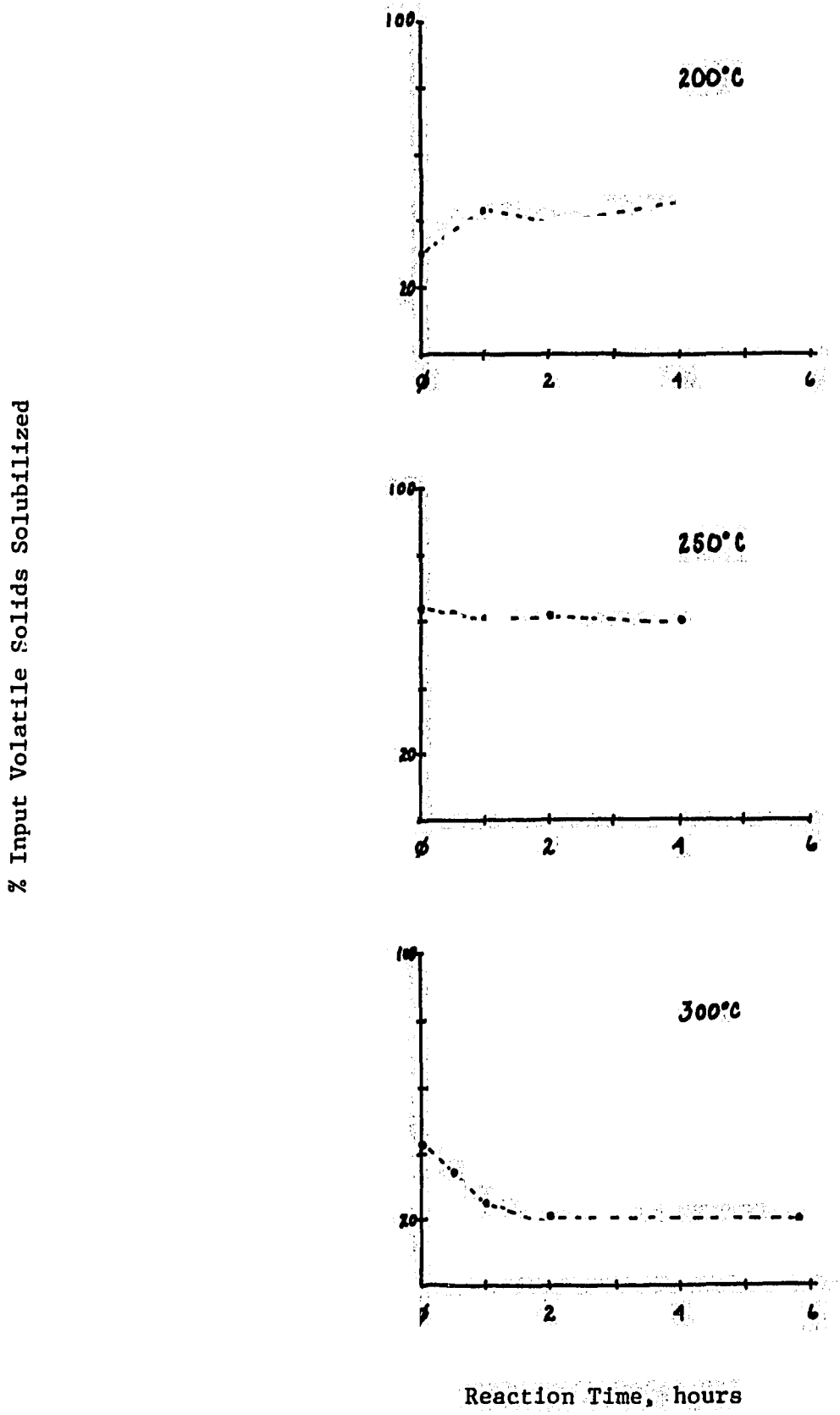
A suspended particle size analysis was performed to determine the physical effects of Na_2CO_3, temperature, and pressure on the lignite. This was accomplished by analyzing pretreatment samples using scanning electron microscopy (SEM). The specifications of the analysis are as follows: treatment 020031, 8% volatile solids loading, and 0.2 gms Na_2CO_2/gm VS. Samples were taken before carbonate addition after carbonate addition, and at T = 150°C, 200°C and 250°C. A variety of magnifications ranging from x11 to x3200 were used on each sample. First, general particle size distribution was investigated. Then, the analysis concentrated on specific particles to determine the change in physical shape as the treatment progressed. In general, it was shown that although particle size distribution remained constant, particle texture and shape was affected by the treatment. Before the treatment, particles were smoother and more geometric in shape whereas samples at 200°C and 255°C were chipped, rough, crusty, and much less geometric. An Elemental Distribution Analysis by X-ray (EDAX) was performed on the samples. It is interesting to note that over time there is a decrease of sodium on the particles (corresponding to the "crust") which may have indicate a leaching of entrapped ions. Elements found in later stages of treatment include silicon, phosphorus, sulfur, calcium, and small amounts of sodium. The collection of micrographs is included in Appendix B.

3.4.3 Solubilization

For each of the experiments, the interim samples were analyzed to determine the percent solubilization of input volatile solids which was effected by the treatment. The percent solubilization was calculated on the basis of the change in volatile solids distribution after centrifugation of a pre-treatment slurry (i.e., lignite, alkali, and water) and a post-treatment sample. The results are represented graphically in Figure 3.3 and summarized in the following.

Figure 3.3

Lignite Solubilization With Sodium Carbonate



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Comparison of the solubilization behavior within each temperature experiment yields dissimilar trends at the three different temperatures. In the 200°C experiment, successive time samples show an increase in the volatile solids solubilized from 30% at temperature to a maximum of 53% after 4.0 hours. The percent volatile solids solubilized in the 250°C experiment remained relatively constant throughout the course of the experiment having reached a 63% maximum at temperature. Finally, in the 300°C experiment, the observed solubilization decreased over time with a high of 43% volatile solids solubilized at temperature falling to a low of 17% after 5.75 hours. On the basis of these solubilization figures, the ideal temperature for hydrolytic breakdown under the conditions as specified is 250°C, with extended treatment times having an insignificant influence.

A possible explanation for the observed behavior can be realized upon examining the competing chemistries involved. It has been established (see Dynatech Report No. 2244, Wise et al., 1983) that two processes are evident here: (1) alkaline hydrolysis of the ethereal lignite matrix to yield low molecular weight aromatic material, and (2) repolymerization of free radical reaction intermediates to yield high molecular weight coalified solids. In light of the experimental results it would appear that temperature and time can both affect the degree to which either of the competing reactions occurs. During a 200°C treatment, hydrolysis seems to predominate, while during a 300°C treatment repolymerization predominates. In the 250°C experiment, the explanation is less obvious. At extended reaction times, an increase in hydrolysis does not seem evident and repolymerization appears controlled.

3.4.4 Acid Precipitation

The product slurries from each of the temperature/time experiments were initially separated into the base-soluble and base-insoluble fractions. This allowed for the determination of the percent of input volatile solids solubilized as detailed in the preceding section. The procedure can effectively identify the amount of water-soluble species of low molecular weight material which was produced via the hydrolysis.

The solubilized material - particularly the volatile solids - can be further characterized on the basis of its behavior in acidic media. Because of the structural characteristics of the input lignite and the hydrolytic nature of the reaction process, the solubilized material is expected to be high in polar functional groups, such as aromatic hydroxy and carboxylic acid groups. While this material would remain in solution in a product slurry of pH 10, acidification should precipitate some of the solids to allow for further characterization and identification.

The alkaline solution containing dissolved products was separated from any solids that were suspended in the reaction slurry. This solution was subsequently acidified to pH 2.0 with concentrated hydrochloric acid. An experimental maneuver such as this is intended for laboratory identifications only; by no means is it intended for eventual process work. Acidification is an effective method of isolation for low molecular weight breakdown material of characteristic oxygen functionality. The procedure provides sufficient solid for subsequent analytical work.

The data corresponding to the acidifications are presented in Table 3.1. The four columns in the table identify the following: (1) the sample; (2) the percent of input volatile solids solubilized (shown graphically in Figure 3.3); (3) the percent of the solubilized volatile solids which can be precipitated by acid; and (4) the percent which the latter, i.e., (3), is of the input volatile material. The results indicate that in the majority of the samples virtually all of the solubilized material can be precipitated by acid. This is particularly true for the 200°C and 250°C treatments in which greater than 96% of the solubilized volatile solids were precipitated. With the samples from the 300°C treatment a substantial percentage (>82%) of the solubilized solid was isolable after acidification; the cases where the yield was low correspond to samples in which solubilization was also low. It appears, then, that acidification is an effective experimental procedure if isolation of breakdown material is desired. This method was exploited for the large-scale collection of treatment products.

Table 3.1

ACID PRECIPITATION

SAMPLE		INPUT VOLATILE SOLIDS SOLUBILIZED (%)	ACID-PRECIPIABLE SOLUBILIZED VOLATILE SOLIDS (%)	ACID-PRECIPITABLE INPUT VOLATILE SOLIDS (%)
Temp	Time			
200°C	0 h	30	99	30
	1	45	99	45
	2	42	97	41
	4	53	99	52
250°C	0 h	63	96	60
	1/2	63	97	61
	1	61	97	59
	2	64	97	62
	4	63	96	60
300°C	0 h	43	93	40
	1/2	34	93	40
	1	25	91	23
	2	22	82	18
	5 3/4	17	86	15

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3.4.5 Extraction

The low molecular weight material which is produced in the lignite hydrolysis can be further characterized in terms of its solubility in organic solvents, i.e., its "extractability." Generally, tetrahydrofuran (THF) is used as the organic solvent because its reasonably low polarity allows the separation of low molecular weight, non-polar material from a complex product slurry. The product mixture will contain many compounds of dramatically different polarities. Extraction with THF can be used to differentiate products on the basis of polarity.

In this work, product solids were subjected to two different extractions for comparison as shown in Figure 3.4. For the first case, a pellet (1) was isolated from a centrifuged slurry sample which had been acidified (pH 2.0) in toto. For the second, the pellet (2) was obtained from an acidified supernatant only. Pellet (1) is representative of all possible product solids because the isolation protocol includes insoluble product residues. Alternatively, pellet (2) contains only that material solubilized in the hydrolysis. It would seem likely that most of the more non-polar, THF-extractable material would be available in pellet (1). Pellet (2) is primarily aromatic material of characteristic oxygen functionality which tends to be slightly more polar. It is important to note that the material of pellet (2) would be entirely contained within pellet (1).

The results of the extractions are presented graphically in Figure 3.5. The percent extractables relative to pellet total solids are shown for both pellet (1) and pellet (2). The trends in the extraction behaviors can be interpreted in terms of the competing reaction chemistries, in much the same way as those on the solubilizations were. In those cases where a greater percentage of extracted material is in pellet (2) - rather than pellet (1) - it would appear that more of the extractable products are solubilized, low molecular weight compounds of reasonably low polarity with

Figure 3.4

Flow Chart for THF Extractions

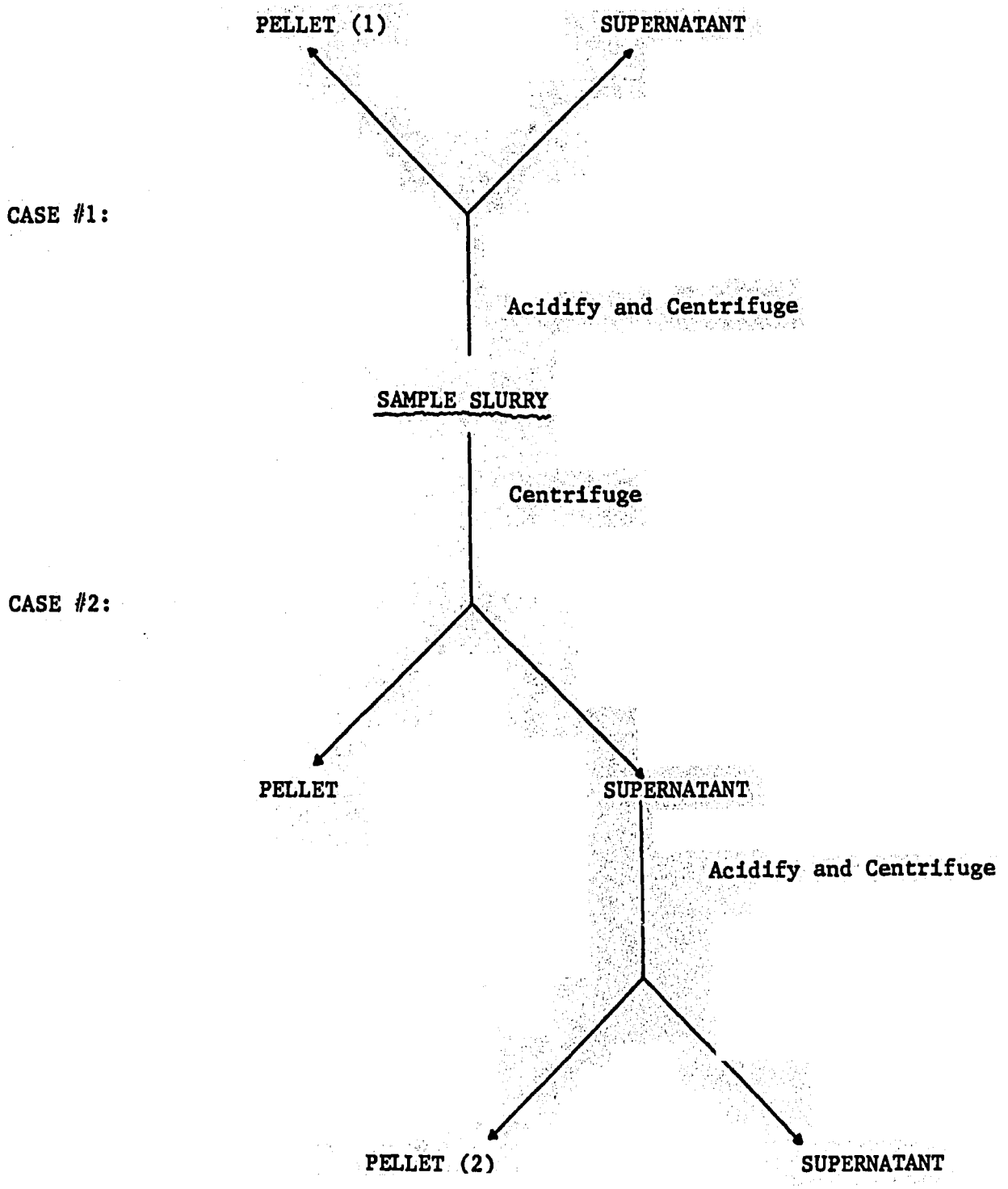

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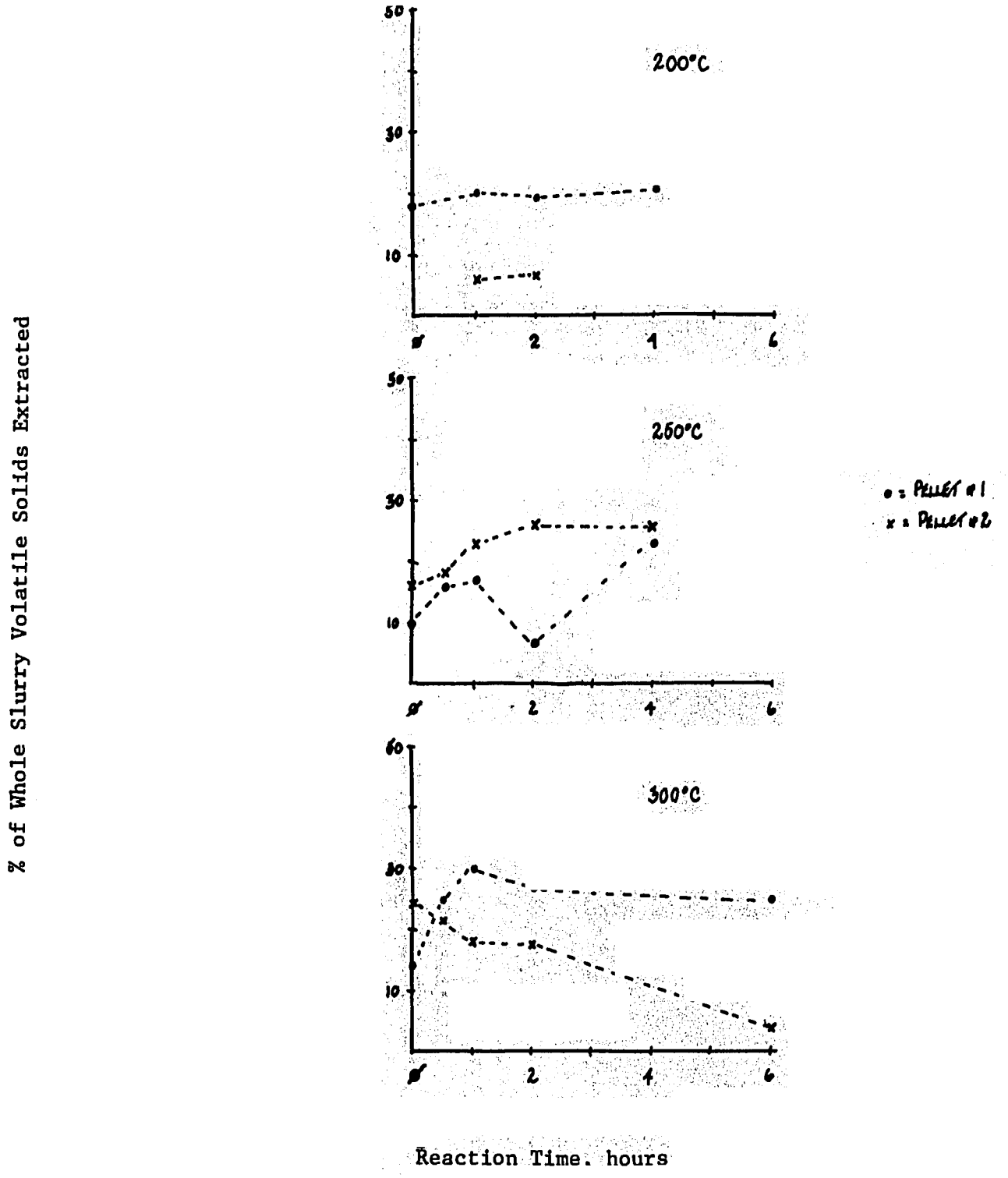
Figure 3.5

THF-Extractable Pellet Solids



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repolymerized macromolecules comprising a major portion of the original reaction residue. Alternatively, when the greater percentage of extracted material is in pellet (1), it would appear that much of the breakdown material is water-insoluble, low molecular weight product which is sufficiently non-polar to allow for extraction by THF. The relative distributions of the various product types are a direct result of the hydrolysis and the repolymerization.

With the 200°C treatment it would appear that most of the extractable material produced initially is the water-insoluble solid which is of reasonably low molecular weight (molecular weight data follows); the solubilized material is not amenable to extraction. The extractables from the 250°C treatment, on the other hand, can be found primarily in the solubilized product fraction which arises from the hydrolysis; the reaction residue contributes very little to the extractables. This phenomenon was time-dependent with percent extractables increasing over time. Extraction of the products from the 300°C treatment was greatest with the reaction residues rather than the solubilized material. This behavior also showed some time-dependence. Extraction of the residue increased over time while that of the solubilized material decreased.

In comparing these results with those on the solubilization, it seems that there may be some compatible trends in the reaction chemistry which can inferred from the data. The results suggest that in those cases where hydrolysis is the predominant chemistry the percent solubilization is highest and the greater percentage of extractable product is in that solubilized material (e.g., the 250°C treatment). Alternatively, when repolymerization successfully competes with hydrolysis, the percent solubilization is lower and the majority of the extractable product is in the reaction residue.

The extracted materials were characterized with respect to the molecular weight distribution. This provides some verification of predicted product characteristics. Gel permeation chromatography (GPC) was used to

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obtain molecular weight profiles for each of the extracts. Generally, the extraction was effective in separating products of molecular weight less than 1000 with the 50-500 molecular weight range being the predominant one. The GPC profiles that are presented in Figure 3.6 are illustrative of the tracings obtained with each of the extracts. The GPC data shown is for a series of extracts of pellet (1)'s from a 200°C treatment.

3.4.6 Additive Studies

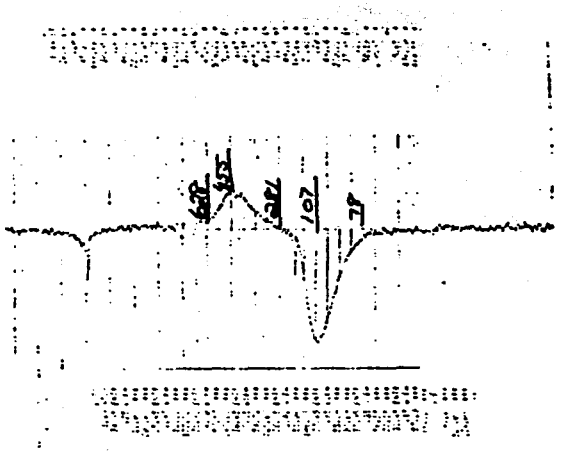
A series of experiments was conducted to investigate the role of the sodium carbonate in the alkaline hydrolysis. Previous work by Dynatech scientists investigating the role of the carbonate in the solubilization of peat had established some of the importance of the sodium cation in successful hydrolyses. In addition, modern knowledge in liquefaction science supports the idea that the size of a sodium cation makes possible diffusion into lignite pores; thus, the cation acts in both the physical and chemical breakdown of lignite. The strong implication that sodium has a major role in the alkaline hydrolysis influenced the direction of this phase of the experimental program.

Three experiments were conducted at 300°C. Using the standard format for reactor loadings, a slurry was prepared which contained lignite, water, and either nothing or one of the following: (1) sodium carbonate or (2) sodium hydroxide. The obvious difference in each of these input slurries is the pre-treatment pH. An initial assumption might then have been that the sodium hydroxide (at an initial pH of 12.0) would be the most effective in promoting the hydrolysis. The pH of the starting and the interim samples is shown in Table 3.2.

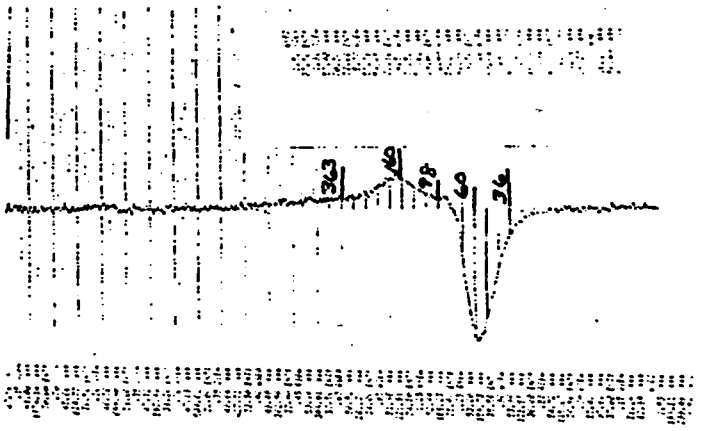
The results of each of the different additive treatments were interpreted in terms of the percent solubilization of input volatile solids, as well as in terms of physical appearance. As far as physical appearance, the final product slurries of 300°C solubilizations with Na_2CO_3, NaOH, and no added base, compare as follows.

Figure 3.6

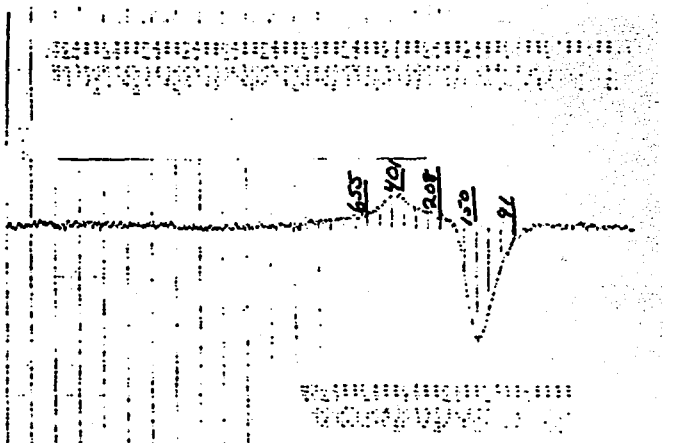
GPC Tracings of Pellet Extracts



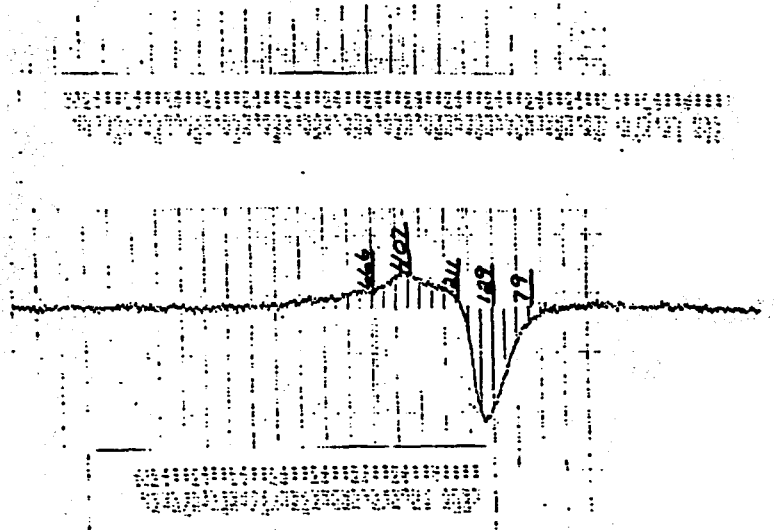
200°C–at temperature



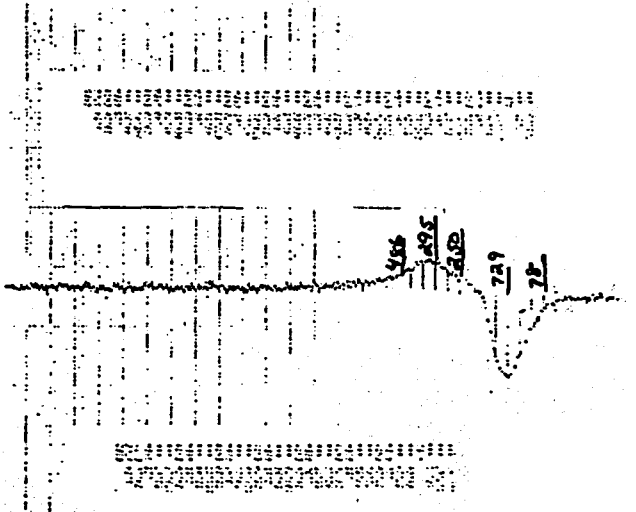
200°C–1/2 hour



200°C–1 hour



200°C–2 hours



200°C–4 hours

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Table 3.2

ADDITIVES AND pH

ADDITIVE	TIME, hr	pH
Sodium Carbonate	input	10.10
	0	10.07
	0.5	9.87
	1.0	9.73
	2.0	9.59
	5.75	9.23
Sodium Hydroxide	input	12.02
	0	10.25
	2.0	10.59
	4.0	10.12
None	input	7.85
	0	7.80
	1.0	7.50
	3.0	7.60

The product from 300°C solubilization in the presence of Na_2CO_3 is a slightly brownish grey/black mobile liquid which throws a solids layer on standing. The product from NaOH-assisted treatment differs essentially only by being much browner. Both these products are sub-visibly particulate. By contrast, the product from a no-base-present treatment is a pure grey/black, with no trace of brown tint. No solids layer is observed to form on standing, yet, the slurry consists of macroscopic, easily visible particles. All three products generate rapidly spreading surface films when dropped into water, including throwing the film upwards from a submerged drop (indicative of hydrophobic constituents). This film expands rapidly to stable final size in the case of the NaOH and no-base products, but shrinks after initial spread with the Na_2CO_3 product, as if an initially hydrophobic layer dispersed into the water over time. The Na_2CO_3-and NaOH-generated products had similar odors, but the no-base product slurry was considerably blander, though not odorless.

The solubilization data are presented graphically in Figure 3.7. In terms of percent solubilization, there are obvious differences in the effectiveness of the treatments. Without any additive, there was no evidence of matrix breakdown. The same was true in the case where sodium hydroxide was added. The most efficient treatment, then, was in the sodium carbonate case. The interpretation of the data is not obvious on the basis of solubilization only. These would appear to be no reason a priori as to why sodium hydroxide was ineffective in promoting hydrolysis.

In addition to the above analyses, the sodium hydroxide and sodium carbonate treatments were evaluated in terms of product extractability. The results are presented in Figure 3.8. The data show trends similar to those of the initial time/temperature work. That is, as solubilization decreases, the percent extractables in pellet (1) increases while that in pellet (2) decreases. It is important to note, however, that in terms of extractability it appears that the sodium hydroxide was effective in generating low molecular weight, water-insoluble product.

Figure 3.7

Lignite Solubilization With Various Additives

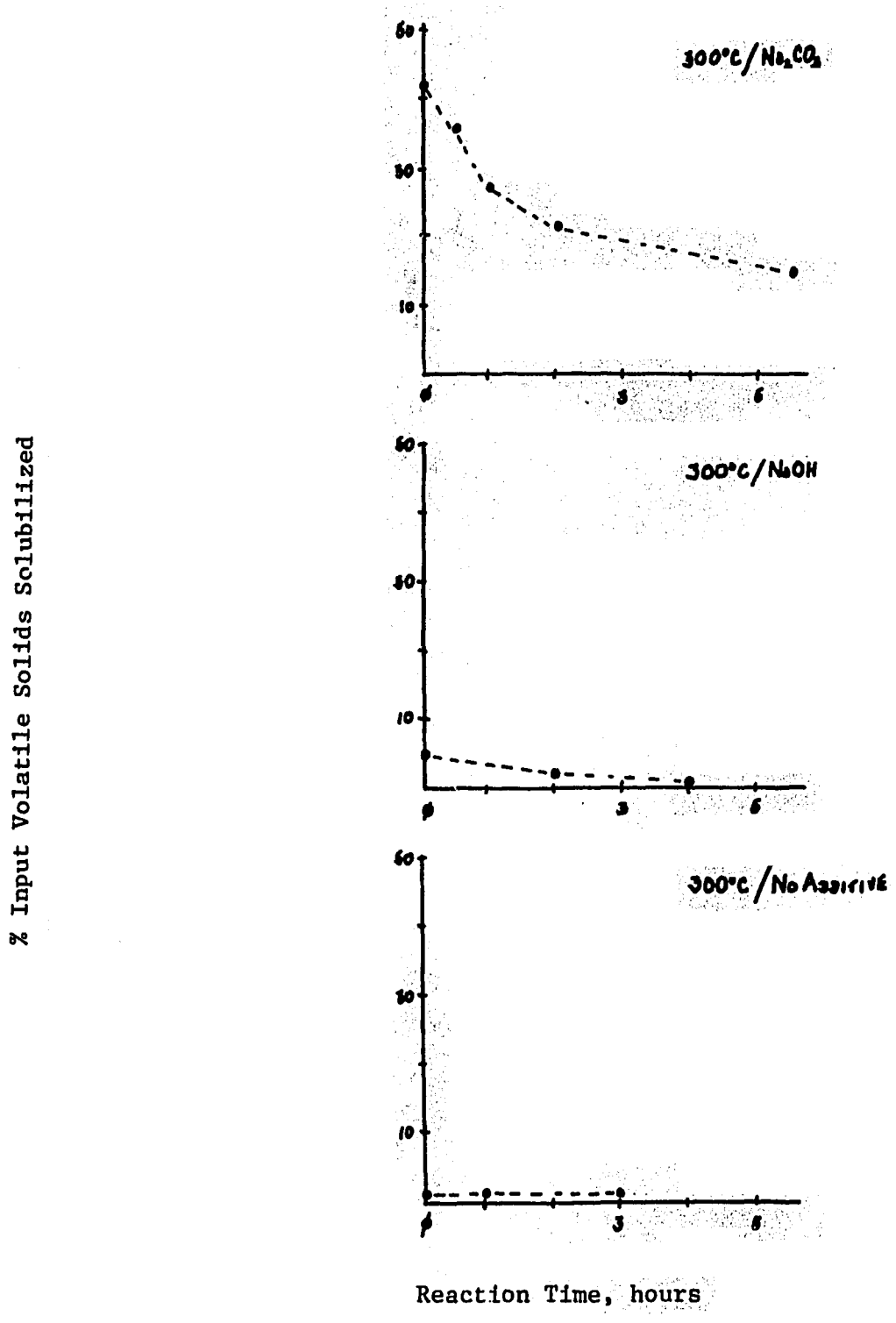

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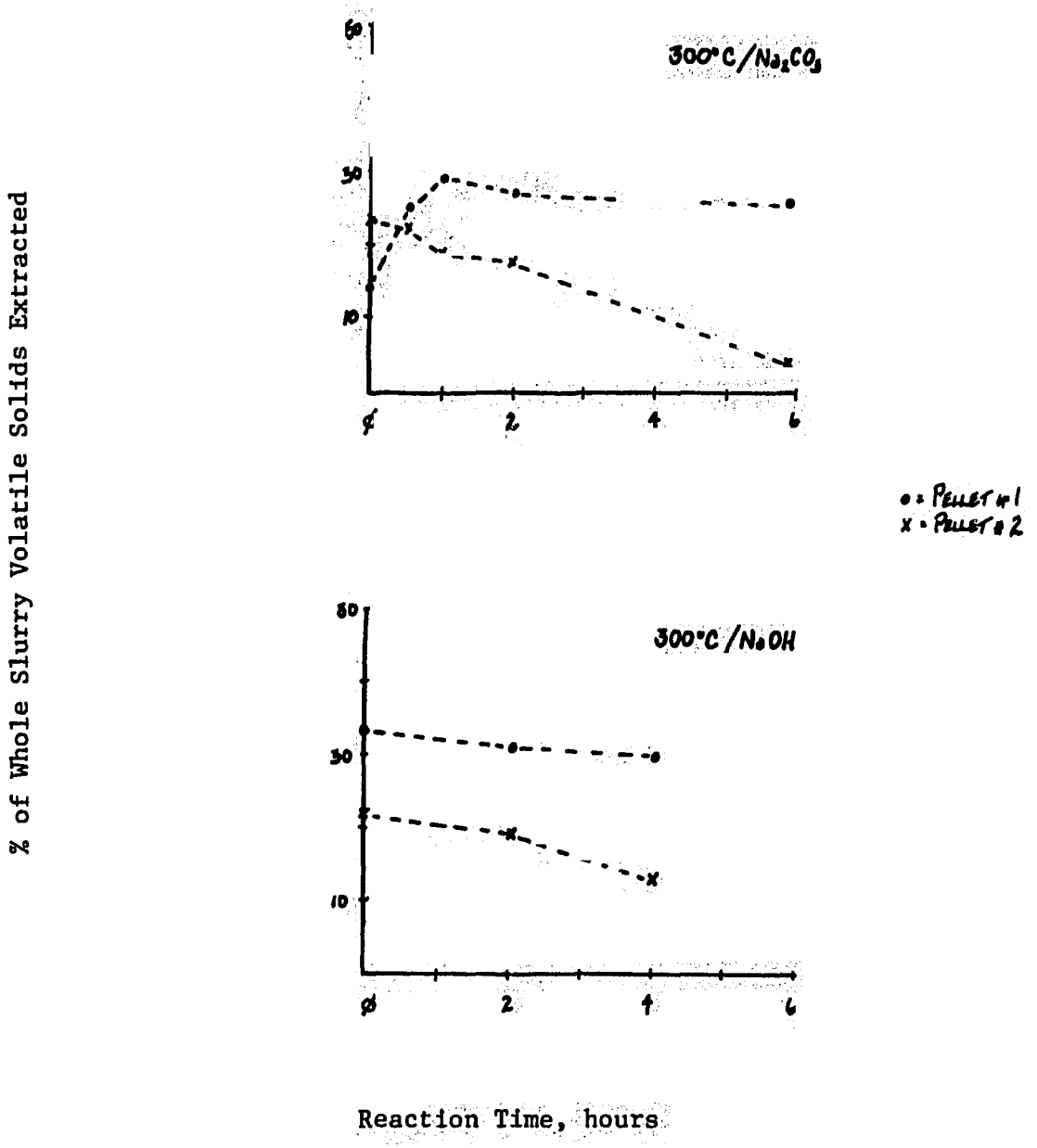
Figure 3.8

THF-Extractable Pellet Solids: Additive Variations



3.4.7 Oxidation Experiments

Table 3.3 shows the conditions for the oxidations in this series of experiments and the %VS solubilized as a result of oxidation. The %VS in the first supernatant decreases significantly in all cases as the oxidation proceeds. However, the %TS remains the same. Apparently, the oxidation is causing precipitation of the volatile solids solubilized. Table 3.4 shows the %VS in the whole slurry and in the first supernatant. Although both categories show some decreases, the %VS in the whole slurry decreases only very gradually. On the other hand, the %VS solubilized shows a large and sharp decrease as soon as the first sample in drawn. This implies that the solubilized volatile solids are susceptible to oxidation in a way other than combustion. The second set of oxidation experiments was designed to test this theory.

Table 3.5 compares the volatile solids data from the separate oxidations of solubilized materials and of non-solubilized materials. Again, the %VS solubilized decreases during oxidation of each type of slurry, while the %TS remains virtually constant. In addition, the %VS solubilized decreases sharply once oxidation of the solubilized material begins, as observed in the previous series of experiments.

The %VS solubilized does not decrease as drastically in the oxidation of non-solubilized material as with the solubilized material. This confirms the theory that solubilized materials are more susceptible to oxidation phenomena than non-solubilized material. In addition, oxidation does not increase solubilization of non-solubilized material. This implies that a two-stage pretreatment process, consisting of solubilization followed by oxidation, would not significantly increase solubilization above the level obtained by the solubilization alone.

Oxidation within the prescribed pretreatment regime effects the solubilized hydrolysis products rather than the non-solubilized hydrolysis products. Oxidation should promote degradation of the non-solubilized material. Oxidation, however, does not do this, but rather promotes the

Table 3.3

OXIDATION CONDITIONS* AND %VS SOLUBILIZED

CONDITIONS	SAMPLE	%VS SOLUBILIZED
400 mL/min	input (at 200°C)	2.3
	3/4 hr oxidation	0.5
	2 hrs oxidation	0.5
740 mL/min	input (at 200°C)	3.0
	1/2 hr oxidation	0.6
	1 hr oxidation	0.4
	2 hrs oxidation	0.5
	3 hrs oxidation	0.8
1000 mL/min	input (at 200°C)	2.7
	1/2 hr oxidation	0.5
	1 hr oxidation	0.5
	3 hr oxidation	0.7

* Note: All of these oxidations were done at 200°C.

Table 3.4

TOTAL VOLATILE SOLIDS COMPARED TO % VS SOLUBILIZED

SAMPLE	% TOTAL VS	% VS SOLUBILIZED
400 mL/min		
input (at 200°C)	4.5%	2.3%
3/4 hr oxidation	4.0	0.5
2 hrs oxidation	2.8	0.5
740 mL/min		
input (at 200°C)	5.1	3.0
1/2 hr oxidation	5.0	0.6
1 hr oxidation	4.6	0.4
2 hrs oxidation	4.9	0.5
3 hrs oxidation	4.7	0.8
1000 mL/min		
input (at 200°C)	5.2	2.7
1/2 hr oxidation	5.0	0.5
1 hr oxidation	4.7	0.5
3 hrs oxidation	4.6	0.7

Table 3.5

VOLATILE SOLIDS DATA FROM OXIDATIONS OF SOLUBILIZED AND NON-SOLUBILIZED MATERIAL

SOLUBILIZED MATERIAL	% TOTAL VS	% VS SOLUBILIZED	%VS sol/ % Tot VS
Input	4.1%	3.1%	0.76
at 200°C	5.6	2.9	0.52
1/2 hr oxidation	3.8	0.1	0.03
1 hr oxidation	3.6	0.1	0.03
2 hrs oxidation	3.3	0.2	0.06

NON-SOLUBILIZED MATERIAL	% TOTAL VS	% VS SOLUBILIZED	%VS sol/ % Tot VS
Input	6.1%	1.2%	0.20
at 200°C	6.0	1.6	0.27
1/2 hr oxidation	5.6	0.8	0.14
81 min oxidation	5.5	0.8	0.15
155 min oxidation	5.2	1.1	0.21

prescription of solubilized hydrolyses product. There are two possible explanation for this: (1) oxidation encourages repolymerization via free radical reaction, or (2) oxidation encourges precipitation via surface charring and agglomeration. In addition, oxidative degradation of non-solubilized material is most likely ineffectual on the "coalified" hydrolysis product (see Table 3.5). Further investigation may be interesting, particularly within the format of the proposed pilot facility which is capable of "fast reaction kinetics" (see Section 5).

Section 4

DECARBOXYLATION OF AROMATIC CARBOXYLIC ACIDS

4.1 Background

The initial products of alkaline oxidation are aromatic aldehydes, alcohols, and carboxylic acids with methoxy side-chains. Low molecular weight alkyl carboxylic acids are also formed. These products are depicted in Figure 4.1. Further oxidation leads to degradation of the aromatic nuclei. The methoxy content of the product also decreases with time, ostensibly due to the elimination of side-chains from the aromatic nuclei.

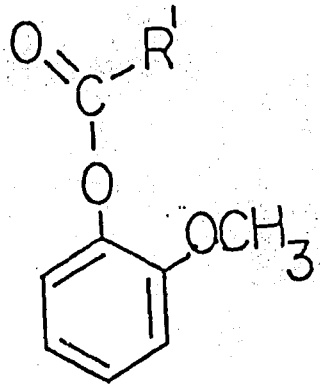
4.1.1 Recovery of Aromatics

Systems for the recovery of the aromatic products are of many different types. Solvent extraction of organic chemicals such as aromatic organic acids from aqueous solution is a technique which has been under consideration for some years. Ethyl acetate, along with diethyl ether, has been suggested as an efficient extraction medium at low acid concentrations. Recently, novel solvent extraction media were developed. This new technology is based on the use of trioctylphosphine oxide in combination with other solvents (Helsel and Dence, 1975). Higher molecular weight acids (butyric or larger) can be efficiently extracted into a liquid hydrocarbon solvent such as kerosene. It would be anticipated that aromatic organic acids could be similarly extractable.

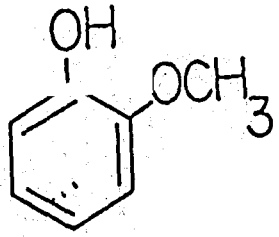
An alternate approach to conventional solvent extraction followed by distillation is solvent extraction followed by re-extraction into an aqueous base. This technique had been successfully employed at Dynatech in work concerned with liquid fuels production from biomass. Organic acids butyric and higher are selectively extracted and concentrated in aqueous base. Concentrations of acid salts obtained in the aqueous base have exceeded 1.0 N. Other approaches to recovery of the aromatic organic

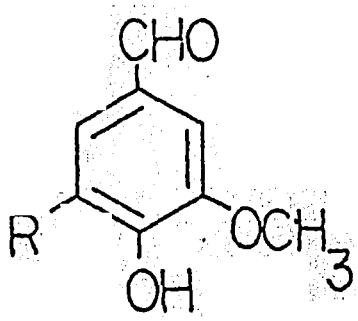
Figure 4.1

MODEL COMPOUNDS
(ALKALINE OXIDATION PRODUCTS)



RCOOH





WHERE

$R' = H$ OR CH_2OH

$R = H$ OR $[CH_3]_3C$ OR OCH_3

160

acids include the addition of an inorganic acid, such as HCl, resulting in the direct precipitation of the aromatic.

4.1.2 Decarboxylation of Aromatic Carboxylic Acids

It has been known for a long time that organic carboxylic acids, particularly aromatic carboxylic acids can be decarboxylated by heating their salts with excess alkali to produce the parent hydrocarbon. The over-all reaction is presumed to be:

$$RCOO^- M^+ + M^+OH^- \xrightarrow{\Delta} R\text{-}H + M_2CO_3$$

Kerkovines and Dimrath (1913) found that aromatic carboxylic acids obtained from oxidation of charcoal could be decarboxylated efficiently by heating their barium salts. Shortly thereafter, Fisher (1919, 1921a, 1921b) found that the sodium salts of aromatic carboxylic acids made from coal oxidation could be decarboxylated by heating them with water to approximately 450°C under pressure. Juettner and others (1935) found that Fisher's method could be used to obtain up to a 94 percent yield from a pure sample of aromatic carboxylic acids. Entel (1955) found that the decarboxylation of aromatic acids produced by alkaline oxidation of coal could be carried out at 250°C if the copper salts were used. It is interesting to note that he was able to effect 96-99 percent decarboxylation by this method. Subsequently, workers at Dow Chemical Company (Montgomery and Holly, 1956, 1958) decarboxylated the copper salts of these acids at 265°C using quinoline as a catalyst and claimed improved results. The results of the product analysis resulting from the copper-quinoline decarboxylation of aromatic acids obtained from the alkaline oxidation of Pocahontas No. 3 bituminous coal are presented in Table 4.1. This has related interest to both peat and lignite.

The results of other workers indicate that nearly quantitative decarboxylation is possible by a variety of techniques. A choice betwen these techniques can be made on economic considerations. It is quite possible that decarboxylation of water soluble aromatic acids will be

Table 4.1

PRODUCT ANALYSIS OF DECARBOXYLATED AROMATIC ACIDS*

COMPOUND	YIELD† g/kg	PORTION OF TOTAL NUCLEI†† %	COMPOUND	YIELD† g/kg	PORTION OF TOTAL NUCLEI†† %
Mass 280	*	-	Benzophenone	7.6	1.7
Mass 268	*	-	Phenanthrene	15	3.3
Mass 260	*	-	Mass 178 (not phenanthrene)	*	-
Mass 258	*	-	Mass 176 (C_7-benzene)	0.7	0.2
Mass 254	*	-	Methylbiphenyl	2.8	0.6
Mass 244	0.007	0.002	Mass 166	0.3	0.07
Mass 234	*	-	Mass 160	0.5	0.1
Mass 232	*	-	Mass 158	*	-
Terphenyl (m- and p-)	5.6	1.2	Biphenyl	41	9.0
Mass 228	0.06	0.02	C_5-benzene	8.1	1.8
Mass 226 ($C_{14}H_{16}O_3$)	0.02	0.009	Methylnaphthalene (α and β)	172	38
Mass 220	*	-	Butylbenzene	1.8	0.4
Mass 218	*	-	Naphthalene	15	3.3
Mass 204 (Phenylnaphthalene)	5.4	1.2	Mass 122	0.1	0.02
Mass 202 (Not fused aromatic ring system)	2.1	0.5	C_2-benzene	0.2	0.04
Mass 196	0.9	0.2	Toluene	3.4	0.75
Mass 184 ($C_{14}H_{16}$)	0.7	0.2	Benzene	91.4	20.0

* Present † Total yield 378 g/kg †† Total of all portions 83 per cent.

*from Montgomery and Holly, 1958.

feasible with peat and lignite hydrolysis products; thus, yielding a BTX-type liquid fuel. Alternative methods to recover the aromatics, as described above, should also be practical.

4.2 Program Plan for Decarboxylation of Pretreated Lignite

A carefully planned alkaline hydrolysis can effect a reversal of the coalification process, particularly in the low rank coals. It was expected that this reversal of the coalification would result in considerable degradation of the coal structure into much simpler chemical units. A chemical functionality common to the breakdown products is the carboxylic acid group. It was a goal of this program to remove the carboxylic acid group (via "decarboxylation") from lignite hydrolysis products to yield water-insoluble organics suitable for use as fuel.

One of chemical methods for decarboxylation of aromatic carboxylic acids is the copper-quinoline method. In fact, this technique was demonstrated using coal acids (Montgomery and Holly, 1956). The mechanism by which the acids are decarboxylated is a combination of thermal and chemical actions. The copper salts of the carboxylic acids are combined with quinoline (a high-238°C-boiling solvent) and heated to reflux. The quinoline facilitates solvolysis, as well as temperature control. The method is closely allied to pure thermal methods in which salts of the acids are heated to 250°C. The copper-quinoline technique was thus chosen for investigation on the basis of its proven success.

Based upon overall applicability to the proposed process, as well as technical and economic considerations, the persulfate/silver ion method of decarboxylation (Fristad et al., 1983) was also chosen for investigation. This method uses sodium persulfate in conjuction with a transition metal catalyst to facilitate carboxylic acid decarboxylation. The sodium persulfate is a powerful oxidant which is relatively inexpensive and easily handled. Its high activation barrier makes the use of persulfate

alone unreasonable at low temperatures. However, when combined with a transition metal catalyst (e.g., a silver ion) the activation barrier of the persulfate ion is reduced and lower reaction temperatures are feasible. In addition, the persulfate serves as an effective electron shuttle to produce active metal species which can participate in the chemical reactions themselves. The mechanism for decarboxylation by the reagent pair is schematicized in Figure 4.2.

Operating on the premise that the major products of the alkaline hydrolysis would be benzoic acid-like, the program plan was to investigate the conditions for decarboxylation of benzoic acid using the persulfate/silver ion method. Maximum operating conditions were to be identified with respect to solvent composition, reagent concentrations, and reaction temperatures. In the final stage of the decarboxylation work, the hydrolysis products of the lignite pretreatment were to be subjected to the "best case" decarboxylation for determination of the percent conversion to water-insoluble organics. The products of the reactions were analyzed by GC, in all cases, and HPLC, in those cases where applicable.

4.3 Decarboxylation of Aromatic Carboxylic Acids - Experimental Procedures

4.3.1 Decarboxylation: The Copper/Quinoline Method

A. Decarboxylation of Benzoic Acid

The procedure used to decarboxylate benzoic acid is a modification of that reported by Buckles and Wheeler (1963) in the synthesis of cis-stilbene from α-phenylcinnamic acid. A 1000-mℓ, three-necked flask is equipped with reflux condenser, magnetic stirrer and thermometer. Benzoic acid (0.205 mol, 25.00 g) and anhydrous cupric sulfate catalyst (.024 mol, 4 g) are added. To this is added freshly-distilled quinoline (2.38 mol, 281

Figure 4.2

Mechanism for Decarboxylation of Organic Acids

$$Ag(I) + S_2O_8^{2-} \rightarrow Ag(II) + SO_4^{-\cdot} + SO_4^{2-} \quad (1)$$

$$Ag(I) + SO_4^{-\cdot} \rightarrow Ag(II) + SO_4^{2-} \quad (2)$$

$$Ag(II) + RCO_2H \rightarrow Ag(I) + RCO_2\cdot + H^+ \quad (3)$$

$$RCO_2\cdot \rightarrow R\cdot + CO_2 \quad (4)$$

$$R\cdot + H\text{-solv} \rightarrow RH + \cdot\text{solv} \quad (5)$$

* From W.E. Fristad et al., 1983.

mℓ) and the system is heated to 210°C using a heating mantle. The temperature of the system is maintained between 210°-225°C for 1.25h after which the flask is cooled and the reaction mixture is gravity-filtered into a 500 mℓ sound-bottomed flask. At this point the reaction mixture smells strongly of benzene. The flask containing the reaction mixture is fitted with a Vigereaux column and the contents are fractionally distilled.

B. Decarboxylation of Benzoic Acid-Time Study

The procedure described in (A) is repeated with the exception that the amount of each reagent is reduced by 50 percent. Samples of the reaction mixture are taken before heating, at 100°C, 200°C, and 0.5h, 1.0h, and 1.25h after the temperature reaches 210°C.

4.3.2 Decarboxylation: The Silver/Persulfate Method

A. Decarboxylation of Benzoic Acid

A 250-mℓ three-necked flask is fitted with reflux condenser, addition funnel, thermometer and magnetic stirrer. Benzoic acid (0.14 mol, 15.88g) and silver nitrate (2.6 mmol, 0.4g) are dissolved in a mixture of 100 mℓ acetonitrile and 33 mℓ water. This solution is added to the flask and heated to reflux (78°C). Sodium persulfate (260 mmol, 61.91g) is added to 67 mℓ water and heated to dissolution. The sodium persulfate is added to the reaction flask over a period of 15 minutes. When addition is complete, the flask is allowed to reflux an additional 5 minutes. After cooling, the reaction mixture is a yellow 2-phase liquid. The layers are separated; the upper layer is washed with saturated sodium bicarbonate solution and the bottom later is washed with ether. The reaction mixture is extracted with ether and saturated sodium bicarbonate as described above.

B. Decarboxylation of Lignite Hydrolysis Products

A concentrate of lignite hydrolysis products is obtained as follows. The "best case" slurry (250°C/ϕ time) is separated by centrifugation.

The solubilized organics are precipitated by acidification (conc HCl, pH 2.0) of the supernatant. The organics are isolated by centrifugation and then dried. This material is considered the essence of the lignite hydrolysate and in this best case amounts to about 63% of the input volatile solids.

The decarboxylation procedure described in (A) is followed with the concentrated lignite hydrolysate replacing the benzoic acid. The reactant amounts are as follows: lignite concentrate (5.0 g), sodium persulfate (84 mmol, 20.0 g), silver nitrate (.98 mmol, .15 g).

4.3.3 Chromatographic Methods of Analysis

The volatile organic liquid determinations of decarboxylation products are made via gas chromatography (GC). Other organic determinations are made via high performance liquid chromatography (HPLC).

A. Gas Chromatography

The volatile organic liquid samples in this phase of the program are analyzed using a Varian 3700 gas chromatograph equipped with a Varian Model 2010 flame ionization detector and a Spectra-Physics 4270 printer, plotter, integrator. The separation is carried out on an Alltech stainless steel AT-1000 on Graphpac column (1/4 in x 6 ft; 80/100 mesh). Samples are run under conditions of linear programming over the temperature range 150°- 210°C (10°C/min) with nitrogen as the carrier gas (30 mℓ/min). The injector temperature is set at 220°C, detector temperature at 230°C. Solutions of standards are prepared in ethanol.

B. High Performance Liquid Chromatography

The organic products are analyzed using a Waters (Milford, MA) HPLC system equipped with a M45 solvent delivery system, a U6K injector, a Model R401 differential refractometer, and a Fisher Recordall Series 5000

recorder. Separation is carried out on a Regis Octadecyl Workhorse column (30 cm x 4.6 mm) using CH_3OH/1% CH_3COOH (1:1) as the eluent. Solutions of standards are prepared in eluent.

4.4 Results and Discussion of Decarboxylation Studies

The strategy for using the model compounds in the decarboxylation studies was three-fold. First, it was desirable to reproduce the literature work to serve as a verification of results and as grounds for development of pertinent analytical protocols. Second, it was of interest to determine the sensitivities in various parameters of the decarboxylation operation. Third, it was necessary to generate data for a best case analysis in the preliminary process designs. This approach was justified in view of the complexity of the lignite solubilization material. Once the experimental plan was defined with the model compounds, lignite hydrolysate was subjected to decarboxylation.

4.4.1 Decarboxylation of Benzoic Acid

One of the procedures used to decarboxylate benzoic acid was the copper sulfate/quinoline method. Benzoic acid was heated to reflux in quinoline with copper sulfate added as catyalyst. At the end of the reaction time, the mixture smelled very strongly of benzene. Distillation of this reaction mixture yielded three fractions: (1) 51°-56°C (1.95 g); (2) 56°- 80°C (3.73 g); (3) 80°-200°C (150g).

Gas chromatographic analyses showed the major benzene yield in fractions (1) and (2). Quinoline peaks appeared prominently in all three fractions even though the high boiling point of quinoline would seem to preclude it from distilling at the lower temperature ranges. An attempt was made to remove quinoline from the reaction mixture by dissolving it in 10% HCl before the distillation. This resulted in precipitation of a large amount of black, granular solid (possibly decomposed benzoic acid) in a dark orange solution. After filtration and distillation, GC analyses still showed a predominance of quinoline in the samples. This over-shadowed the benzene analyses making benzene quantitation impossible.

The second procedure which was used in the decarboxylation of benzoic acid was the persulfate/silver ion method. A mixture of benzoic acid and sodium persulfate was heated to reflux in a solution of 50% acetonitrile/water. At the end of the reaction time, the mixture was a two-phase liquid. However, encouraging this two-phase liquid was, a control experiment sine benzoic acid also produced a two-phase liquid. This suggest that the strong oxidizing nature of the reactants may act to promote polymerization and, hence, the H_2O-insolubility of the acetonitrile.

The persulfate/silver on method was investigated with respect to the effects of reactant concentrations and time on yield of benzene. Both phases of the reaction mixtures were analyzed via GC for the presence of benzene. As would be expected, the majority of the benzene which was generated reported to the upper (i.e., the non-aqueous) layer.

The GC analysis of the "base case" decarboxylation (50% acetonitrile/H_2O; 20 minutes) is shown in Figure 4.3. The yield of benzene from this reaction was 38%. A time study of this decarboxylation showed varying yields with time, a maximum benzene yield of 41% achieved at one hour reaction time (Figure 4.4). The decreased yield of benzene at the longer reaction time (i.e., two hours) indicates increasing complexity of reaction under the strong oxidizing conditions.

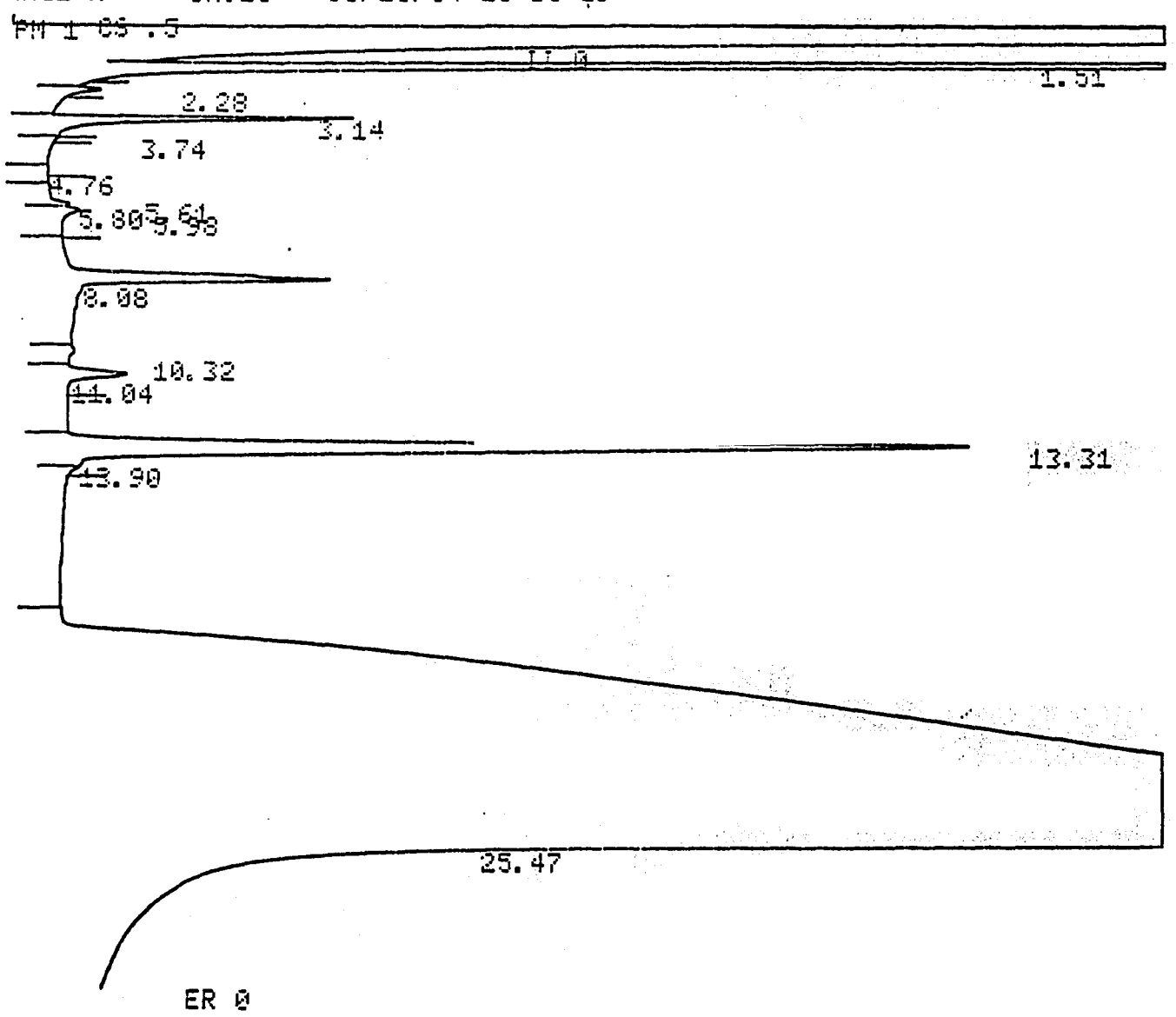
The persulfate/silver ion method of decarboxylation effectively eliminates the use of quinoline, a solvent which is not exceedingly desirable from a process standpoint. The method is simple, fast, and energy conservative. It does, however, call for the use of acetonitrile in the reaction process, another solvent which is not so desirable in a process. The acetonitrile serves as the proton donor (see decarboxylation scheme, Figure 4.2) and this plays an important role in the reaction. Because this work addresses an eventual commercial process it was important to determine how much acetonitrile is necessary for the decarboxylation.

Benzoic acid was subjected to persulfate/silver on decarboxylation in 50:50 acetonitrile/water, 25:75 acetonitrile/water, and 100%

Figure 4.3

GC Analysis: Base Case Decarboxylation

CHANNEL A INJECT 06/26/84 10:30:29



INPUT OVERRANGE AT RT= 0.68

DOE-6-3 06/26/84 10:30:29 CH= "A" PS= 1.

FILE 4. METHOD 5. RUN 20 INDEX 1

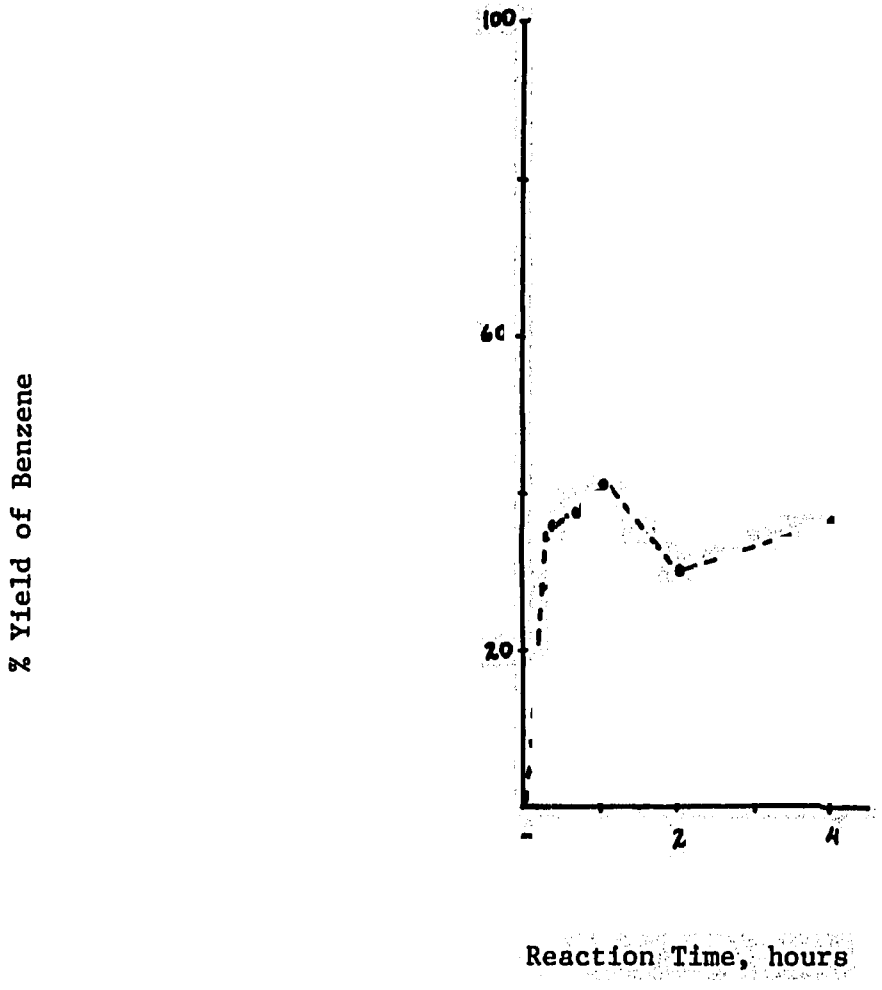
ANALYST: DMH

SAMPLE 1 020407-D

NAME	MMOL/L	RT	AREA	BC	RF	RRT
BENZENE	140.543	1.51	2707306	01	19263.25	1.
TOTALS	140.543		8404518			

Figure 4.4

Time Course for Decarboxylation of Benzoic Acid: Base Case



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water. Relative reactant concentrations are shown in Figure 4.5. A reduction in the amount of acetonitrile had a profound effect on the efficiency of reaction. Whereas in the 50:50 case there was a 36% yield of benzene, in the 25:75 case the yield dropped to 6%. There was negligible decarboxylation under totally aqueous conditions. These results illustrate the need for a donor solvent if reaction is to be effective. However, in the decarboxylation of lignite hydrolysate it may not be necessary to add 50% acetonitrile to the process stream. Some of the products of the alkaline hydrolysis may be effective proton donors themselves (e.g., the phenolic compounds).

4.4.2 Decarboxylation of Lignite Hydrolysate

Lignite hydrolysate was subjected to decarboxylation using the persulfate/silver ion method. Rather than using the entire hydrolysis slurry for the experimental work, only the solubilized organics were used. The hydrolysis slurry was centrifuged, and the resulting supernatant was decanted and acidified. The organic material which was precipitated was isolated upon centrifugation. This material was used because it was assumed to be richest in the carboxylic acid-like product most susceptible to decarboxylation.

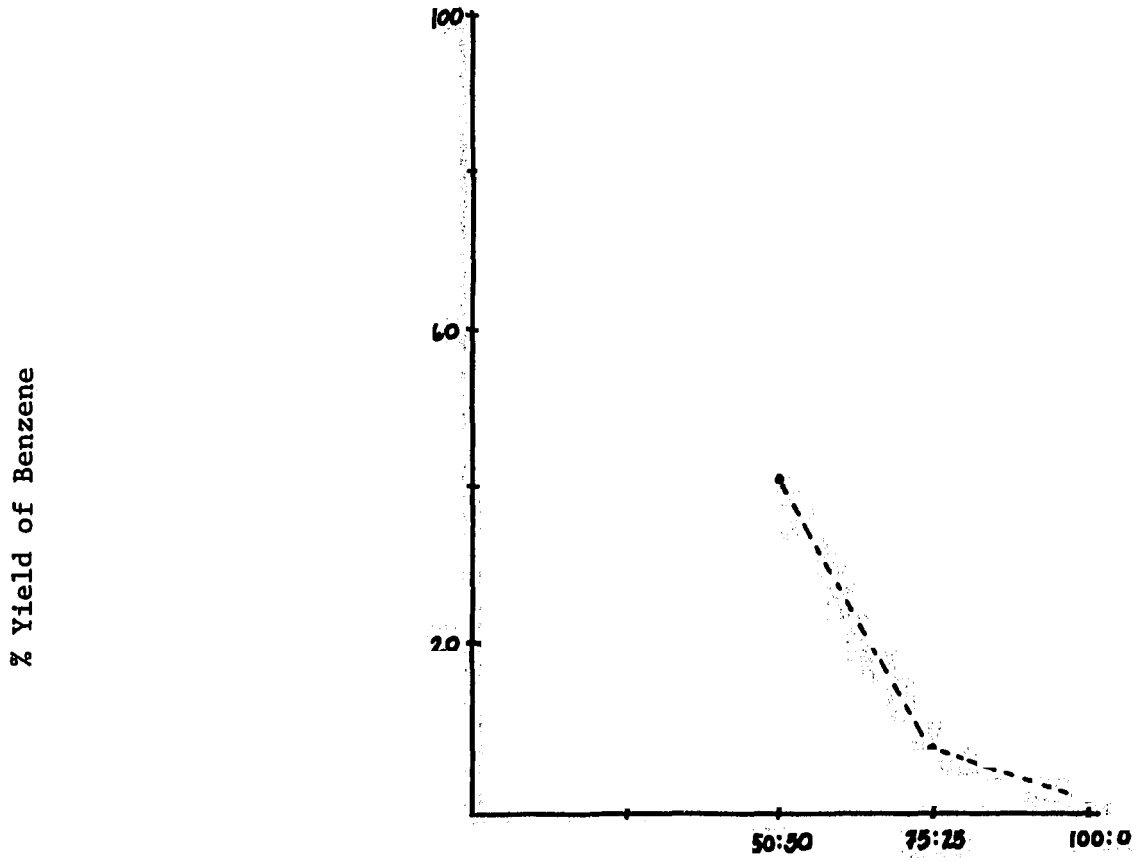
The organic hydrolysate was combined with sodium persulfate and silver nitrate in 50% acetonitrile. The reaction mixture was heated to 100°C in a Parr bomb and cooled. The product was analyzed via GC.

The 6% yield of water-insoluble organic material represents 4% overall conversion of the input lignite volatile solids. This, unto itself, is certainly not so overwhelmingly encouraging for start-up of a full-scale process. It does indicate, though, that there may be some promise for the production of BTX-type liquid fuels from lignite.

The work shown here represents a limited and isolated effort in decarboxylation of a lignite hydrolysate. The products of the hydrolysis

Figure 4.5

Decarboxylation of Benzoic Acid: Acetonitrile/Water Variations



are exceedingly complex. Future work should be directed towards two research areas. One is the extensive identification of the major components of the products of lignite breakdown. If these materials are subject to rigorous characterization and identification, they can be fit more adequately into the decarboxylation scheme. The mechanistic details for decarboxylation of the lignite hydrolysate will be better understood in light of the product identifications. The second area for future research concerns the investigation of the role of the catalyst in the decarboxylation. From a process viewpoint, is is important to identify the form the catalyst must take (e.g., fixed-bed), the lifetime of the catalyst (for purposes of regeneration), and any improvements in catalyst performance. This is a cumbersome task, but one which must be accomplished if the direct liquefaction of lignite is to be considered a viable means of liquid fuels production.

Section 5

THE PILOT - SCALE FACILITY FOR DIRECT LIQUEFACTION OF LIGNITE

The laboratory phase of the liquefaction program illustrated that lignite could be solubilized under conditions of alkaline hydrolysis. The hydrolysate contained aromatic organic acids which are capable of decarboxylation to water-insoluble organics. The experimental program was used to identify some of the necessary processing conditions, such as temperature and alkali concentration, and to characterize the nature of the reacted material. Under batch conditions, maximum lignite solubilization was observed at 250°C, 8% volatile solids loading, and 20% sodium carbonate (weight per weight of lignite volatile solids). The results demonstrated the feasibility of an aqueous treatment of lignite and provided insight into the preliminary design of a pilot-scale facility.

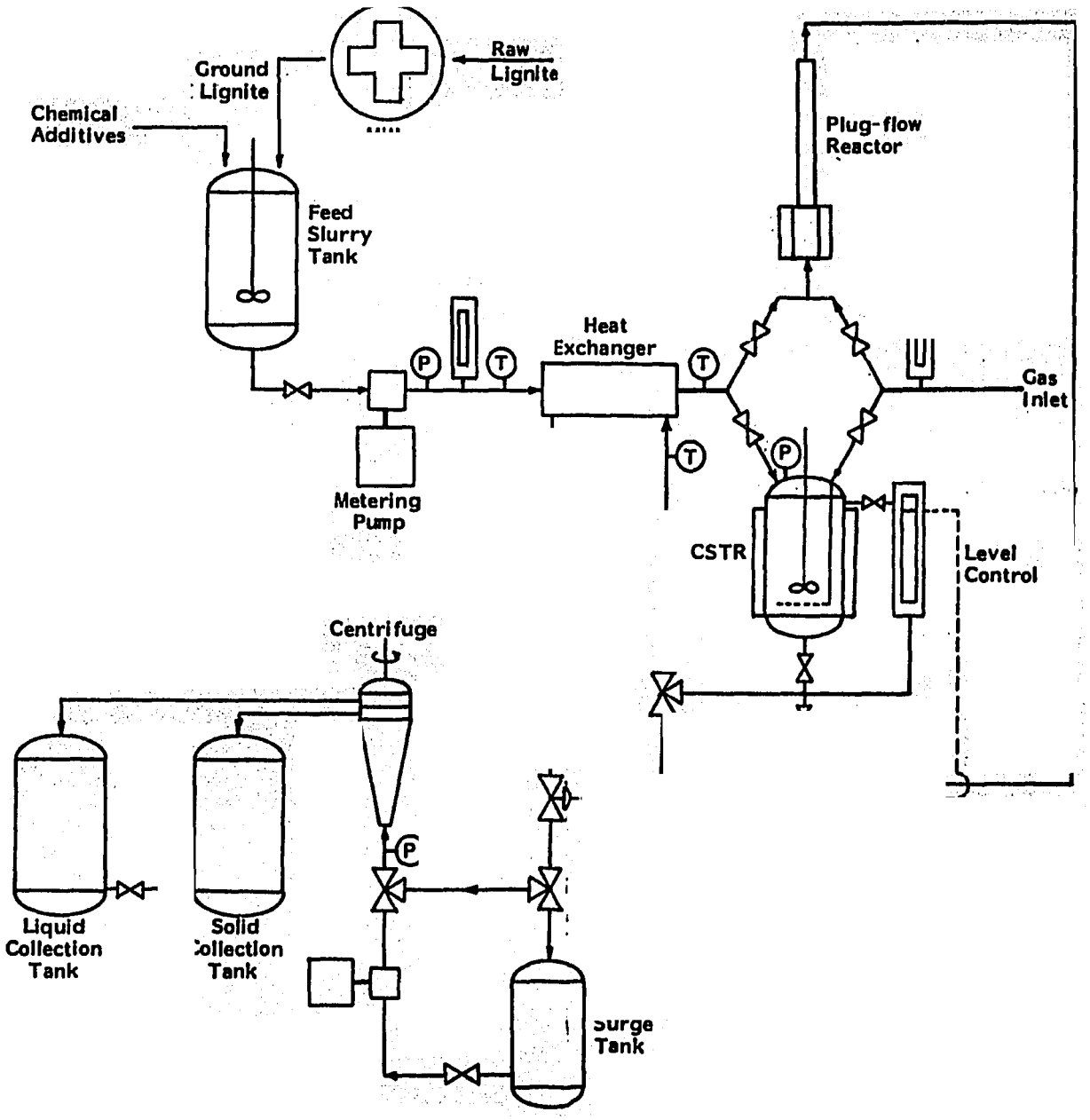
Here, "pilot-scale" is taken to mean an expanded scale laboratory facility. In this light, the pilot phase of the research would concentrate on the more detailed analysis of the alkaline hydrolysis of the lignite in an effort to "optimize" the process. The work would focus on the development of a kinetic model which identifies the reaction time-temperature profiles, as well as the reactant concentrations corresponding to maximum solubilization of the lignite under the "pilot conditions."

5.1 The Reactor System for Lignite Pretreatment

The pretreatment apparatus which was utilized in the laboratory program at Dynatech is a batch reactor system. It is neither sufficiently large for the production of enough extracted material for use in subsequent processing steps, nor is it sufficiently versatile for achieving the short retention times necessary for a detailed kinetic study. Therefore, it is proposed to build a continuous apparatus for the pilot-scale work. This satisfies the scaled-up throughout requirements for investigation of subsequent processing steps, and yields meaningful results for the development of a predictive kinetic model. The apparatus is schematicized in Figure 5.1

Figure 5.1

Preliminary Design for Laboratory Hydrolysis Unit



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Because limited information is currently available which would suggest an appropriate retention time for a continuous system, some preliminary experiments are necessary. For short retention times, on the order of seconds, a plug flow reaction system would seem to be appropriate. For longer reaction times, on the order of minutes, a CSTR would probably be appropriate. The batch system currently in use has a retention time on the order of hours and experiments have indicated that shorter retention times are necessary. Maximum solubilization under batch conditions was achieved when the reaction just reached 250°C - longer reaction times resulted in rapid repolymerization of the reaction intermediates (see Section 3).

The equipment differences between a plug flow reactor and a CSTR are small, except for the reaction chamber itself. The feed tanks, pumps, valving, reactant stream quench and instrumentation are the same for both systems. The plug flow reaction chamber is a jacketed tube which rapidly heats the reaction mixture, and maintains the elevated temperature for a specified time. The CSTR chamber is a jacketed vessel in which the entering stream is heated by mixing with the reacting mixture. In both systems the residence time is adjusted by varying the flow rate of the reactants.

The parameters which would be investigated in this pilot-scale program are temperature, mean residence time, coal concentration and particle size, and chemical additive concentrations. These parameters would be varied, with the objective of developing a predictive model to describe the dynamics of the process, to be used to approximate the optimal design conditions. To cover the broad range of residence times, both the plug flow (1-30 sec residence times) and CSTR (2-60 min residence times) systems could be used.

The kinetic model which would result from the pilot program would indicate the optimal time-temperature profile. This would give some indication as to whether a staged reactor configuration would be appropriate for the overall process design. Staging would be an attractive addition to

the pilot-scale facility since it would offer an advantage in materials handling and potentially add to the yield of desirable product.

5.2 Capital Costs for the Pilot-Scale Pretreatment System.

The pilot-scale pretreatment system schematicized in Figure 5.1 has been designed for a laboratory scale program. The costs for the continuous reaction equipment would be $33,210; for the pertinent glassware the costs would be $3000. The costs are itemized in Table 5.1.

Table 5.1

THE PILOT-SCALE PRETREATMENT SYSTEM

A. CONTINUOUS REACTION EQUIPMENT

	$ AMOUNT
Reactor 26, 1000 psi 600°F (Temp Control)	4,200
Sight	450
Level Control	250
Control Value	300
Centrifuge	12,000
Mill	3,200
Pumps: Feed 200 ml/min 1500 psi	750
Centrifuge 2 l/min	400
Storage Tanks: 10L	70
(3) 20L	330
1L (surge, 1000 psi)	170
Tank Agitator	300
Heat Exchanger (High pressure)	250
Values: (2) 3-Way Ball	210
(1) Metering	50
(8) Ball	600
Gauges: (3) Pressure	50
(8) Temperature	250
(2) Electronic Flow	4,000
(1) Rotameter (Gas)	200
Tubing	300
Assorted Fittings	750
Recording Equipment	1,500
Steam Assembly	2,000
Explosion-proof	630
	$33,210

Table 5.1 (Continued)

B. LABORATORY GLASSWARE	$ AMOUNT
Evaporator	480
Distilling Apparatus	1,010
Heating Mantle	450
Variac	200
Extraction Apparatus	310
Heating Mantle	200
Variac	100
Clamps, Supports, Tubing	250
	$ 3,000

Section 6

THE FULL-SCALE FACILITY FOR DIRECT LIQUEFACTION OF LIGNITE

The results of the laboratory program were used to design a full-scale facility for the direct liquefaction of lignite to BTX-type fuel. The preliminary process design was evaluated by Dr. Ernest E. Kern of Houston Lighting and Power Company, a member of the Industrial/University Review Committee, with the assistance of the engineering staff at Dynatech. The Aspen Plus® (Aspen Technology, Inc., Cambridge, MA) process simulator and economic evaluation system was used to develop a computer model from the preliminary process design. The use of the Aspen Plus® computer program allowed for the calculation of all heat and material balances for the liquefaction process, of all equipment sizing, and of all capital and operating costs.

6.1 Full-Scale Process Design

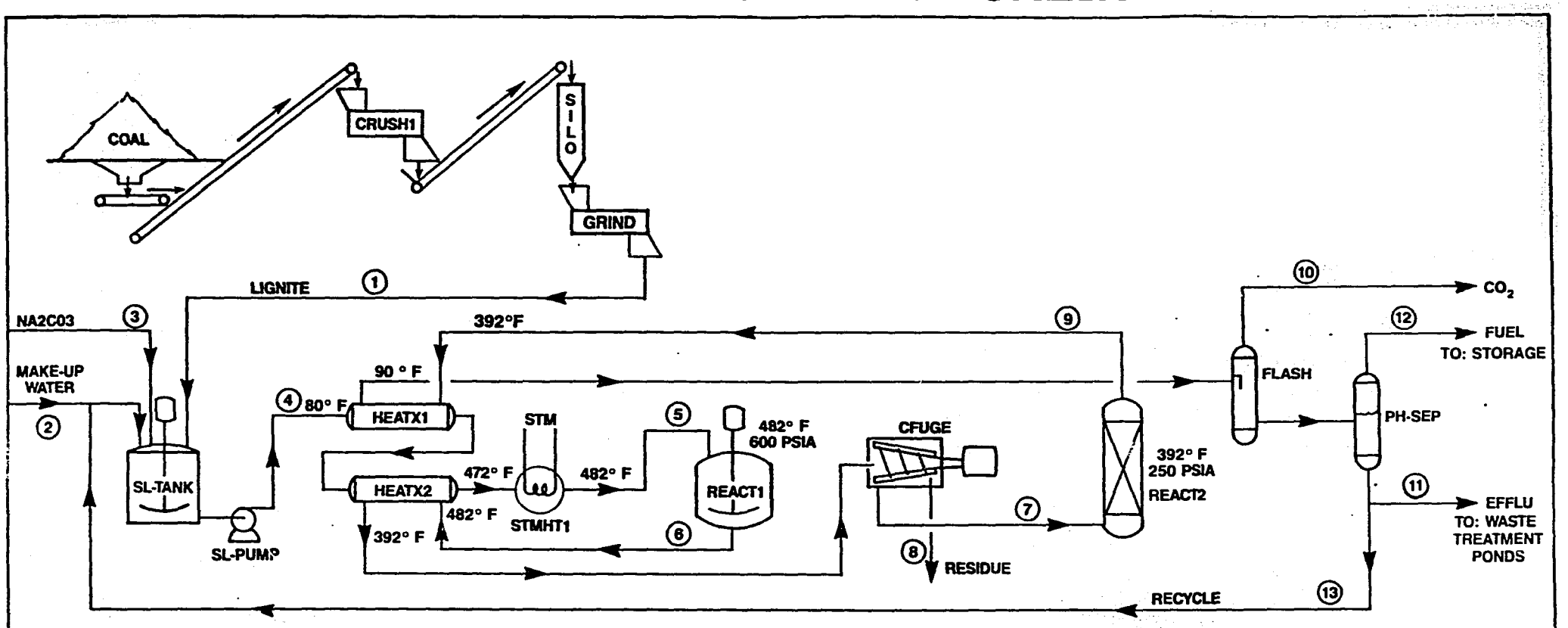
The flowsheet diagram for the liquefaction of lignite to BTX-type fuel is shown in Figure 6.1. The process is depicted as a two-stage chemical treatment. The first step is the alkaline hydrolysis where the complex macromolecular structure of lignite is broken down to water-soluble salts of aromatic acids. The second step is the catalytic decarboxylation where the aromatic acids are converted to water-insoluble organic liquids. Model compounds were used to characterize the product streams. Benzoic acid was chosen to model the products of the first reaction, toluene the products of the second reaction.

The process depicted in Figure 6.1 consists of the following unit operations:

1. Coal Handling (Conveying and Storage);
2. Crusting and Grinding;
3. Slurry Preparation and Handling;
4. Heat Exchange;
5. Alkaline Hydrolysis - Reactor No. 1;
6. Solids Separation (Centrifuge);
7. Decarboxylation - Reactor No. 2;
8. Separations (Gas-Liquid and Liquid-Liquid); and
9. Waste Treatment.

Figure 6.1

BTX—TYPE FUEL FLOWSHEET



BASE CASE 50% RECYCLE — THOUSAND LBS / HR

STR'M ID / COMPONENT	1 LIG'TE	2 WATER	3 NA2C03	4 SLURRY	5 REA1-FD	6 REA1-OUT	7 OVFLW1	8 RESID1	9 REA2-OUT	10 CO2	11 EFFLU	12 BTX-PROD	13 RECYCLE
H20	0	2335	0	4583	4583	5000	4500	500	4500	0	2250	0	2250
CO2	0	0	0	0	0	33	30	3	140	140	0	0	0
ACIDS	0	0	0	152	152	677	610	68	305	0	152	0	152
BTX-FUEL	0	0	0	0	0	0	0	0	230	0	0	230	0
NA2C03	0	0	167	167	167	167	0	167	0	0	0	0	0
COAL	1667	0	0	1667	1667	158	0	158	0	0	0	0	0
ASH	0	0	0	0	0	417	0	417	0	0	0	0	0
RESID	0	0	0	0	0	117	0	117	0	0	0	0	0
TOTAL,000#/HR	1667	2335	167	6568	6568	6569	5140	1429	5175	140	2402	230	2402
TONS/DAY	20000	28020	2000	78821	78821	78829	61676	17146	62098	1679	28826	2760	28825
TEMP. F		72		80	482	482	392		392	90	90	90	90
PRESS. PSI		45		630	600	585	250		235	65	65	65	65

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This process design was detailed in an earlier report (Dynatech Report No. 2282). The conditions for reaction are detailed in Sections 3 and 4. The base case conditions for production of BTX-type fuel can be summarized as in Table 6.1.

The base case heat and material balances are for a 20,000 TPD plant producing 15,000 barrels per day of fuel. The base case costs are shown in Table 6.2. The total capital investment required is estimated to be $644 million at 50% debt. In order to achieve a 17% interest rate of return on equity, it is required that the initial selling price be $8.95 per million BTU's ($1.16 per gallon).

Obviously, the price of $1.16 per gallon is not very competitive in today's marketplace. Prices for No. 2 heating oil and unleaded gasoline are currently around $0.75 per gallon. However, the price of $1.16 per gallon is attractive when compared to alternative coal liquefaction and gasification prices.

6.2 Sensitivity Analysis

The Aspen Plus® program was utilized to get a sensitivity analysis of the initial selling price ($8.95 per million BTU's). The parameters investigated included: slurry solids concentration, lignite price, debt ratios, and heat transfer coefficients. The results are summarized in Table 6.4.

The most profound effect was with the slurry solids concentration. There are higher capital costs for equipment which must handle large volumes of water. A change in the slurry concentration from 27% solids to 8% solids triples the volume of slurry and doubles the equipment cost. This results in an increase of 50% in the selling price of the product.

Increasing the cost of the lignite from $12/ton to $18/ton causes a 12% increase in the product price from $8.95/MKB to $10.06/MKB.

Table 6.1

DIRECT LIQUEFACTION OF LIGNITE TO BTX-TYPE FUEL:
BASE CASE PARAMETERS

Lignite Feed Rate	20,000 TPD
Lignite Heating Value	6,000 BTU/LB
Lignite Price	$12/Ton
Recycle Process Water	50% of Effluent Stream
Reactor-1 Conversion	63% of Volatile Solids
Reactor-2 Conversion	50% of Acids
BTX-Type Fuel Heating Value	18,000 BTU/LB
Interest Rate of Return on Equity	15%
Inflation	7%/Year
Project Start	March 1985
Commercial Production	October 1988
Percent Debt	50%

Table 6.2

BASE CASE RESULTS

INVESTMENT	$ MILLION
Physical Plant	$ 389
Interest During Construction (10%)	37
Start-up	63
Tax Credit	-51
Working Capital	89
Contingency	117
TOTAL	$ 644

SCHEDULE	
Project Start	March 1985
Commercial Production	October 1988

REVENUE	
Capacity Production Rate (Tons/Day)	2760
Normal Production Rate (Tons/Day)	2346
Initial Selling Price ($/Ton 1988)	437
Initial Selling Price ($MKB 1988)	12.14
Initial Selling Price ($MKB 1984)	8.95
Initial Selling Price ($/Gal 1984)	1.16
Return on Investment	17.4%
Payout Time (Years)	5.8

CAPITAL INVESTMENT	$ MILLION
Total Equipment Cost*	123
Total Field Construction Cost	310
Total Depreciable Cost	506
Total Capital	668

ANNUAL OPERATING COST 1988	
Total Raw Materials	148
Total Utilities	25
Waste Treatment	2.9
Catalyst	2.9
Labor	32
Supplies	12
General Works	28
Depreciation	34
Gross Operating Cost	$285

* (See Table 6.3).

Table 6.3

EQUIPMENT COSTS: BASE CASE

ITEM	NO. OF UNITS	DESIGN P, T OR MOTOR SIZE	SIZE EACH	$ x 1000 UNIT PRICE	$ x 1000 TOTAL	$ x 1000 INSTALLED
Coal Hdl Equipment	1	-	20,000 TPD	-	4,669	24,746
Coal Silos	8	-	800 TON	77	612	3,266
Crushers	2	750HP MOTOR	1,500 TPH	147	294	878
Grinders	8	750HP MOTOR	100 TPH	184	1,470	4,390
Slurry Tanks	16	W/75HP AGIT'RS	20,000 GAL	51	821	3,045
Slurry Pumps	16	300HP MOTOR	575 GPM	31	499	1,408
Heat Exchangers	32	650PSI, 500°F	73 MBH	499	15,981	41,441
Steam Heat Exchangers	16	800PSI, 550°F	4.8 MBH	16	257	667
Reactors No. 1	16	650PSI, 500°F	46,000 GAL	495	7,925	26,987
Centrifuges	4	750HP MOTOR	100 TPH	662	2,646	6,648
Reactors No. 2	8	275PSI, 450°F	34,000 GAL	382	3,058	8,477
Flash Tanks	8	75PSI, 150°F	30,000 GAL	81	651	2,361
Phase Separators	8	75PSI, 150°F	30,000 GAL	81	651	2,36L
Storage Tanks	6	75PSI, 150°F	400,000 GAL	99	592	3,159
Waste Water Treatment	1	ATM	-	-	-	9,027
TOTAL					40,126	138,861

Table 6.4

SENSITIVITY ANALYSIS

CASE	LIGNITE PRICE $/TON	PERCENT DEBT %	SLURRY SOLIDS %	EQUIPMENT COST	INVESTMENT PHYSICAL COST	$M TOTAL COST	INITIAL SELLING PRICE		PRESENT VALUE $/MKB	COMMERCIAL PRODUCTION DATE
							$/TON	$/MKB		
A (base case)	12	50	27	123	389	644	437	12.14	8.95	Oct 1988
B	12	0	27	123	389	607	462	12.83	9.46	Oct 1988
C	12	80	27	123	389	666	422	11.72	8.65	Oct 1988
D	18	50	27	123	389	664	491	13.64	10.06	Oct 1988
E	12	50	13	157	512	823	498	13.83	10.03	Dec 1988
F	12	50	8	235	813	1273	681	18.92	13.49	Apr 1989
G (U=150)*	12	50	27	167	543	873	526	14.61	10.60	Jan 1989

Table IV: Results of the case study on the direct liquefaction of lignite using the Aspen Plus® costing model. The effect of lignite price, slurry solids concentration, percent debt and heat transfer coefficient on the initial selling price of the product was determined assuming a 15% interest rate of return on equity.

* Heat Transfer Coefficient U=350 Btu/hr·Ft^2·°F in all other cases.

The financing of the plant using different debt ratios also has a profound effect on the selling price of the product. For percent debts of 0, 50, and 80 percent, the risks of the project are shared in construction years, but so are profits in subsequent years. Selling prices are $8.95/MKB for 50%, $9.46/MKB for 0%, and $8.65/MKB for 80% debt ratio at $12/ton lignite and 27% solids.

The heat transfer coefficient was used to size the heat exchangers. The heat exchangers are the single most expensive item on the equipment list (see Table 6.3). Lowering the heat transfer coefficient from 350 to 150 BTU/hr•sqft•°F increases the number of heat exchangers from 48 to 128. The total equipment cost increases from $123 million to $ 167 million. This increases the fuel cost 18%.

Section 7

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Appendix A

COAL ANALYSIS REPORTS

As Submitted By:

Resource Engineering Incorporated
Waltham, MA 02154

The following reports detail the ultimate, proximate and petrographic analyses of the original lignite samples and the pretreated lignite samples from this experimental program. The original lignite samples were obtained from the Buelah mine and are identified as R455 (9/13/82), A790 (6/7/83), and A942, (11/28/83). The pretreated lignite samples were residues from a 300°C/0.5 hour and a 100°C/21 day hydrolysis. These are identified as A817 and R486 (both 300°C treatments) and A895 (a 100°C treatment). The analyses are presented chronologically as reported, along with pertinent correspondence from the REI technical staff.

Resource Engineering Incorporated

80 Bacon Street, Waltham, Massachusetts 02154 (617) 894-6720

Sept. 13, 1982

Dr. Donald L. Wise
Vice President
Dynatech R/D Company
99 Erie Street
Cambridge, MA 02139

Dear Don,

It was quite interesting to meet with David S. Gleason. He seemed to have a positive view of what has been done, as far as I could determine.

Attached is the report of the petrographic data we discussed during Mr. Gleason's visit of the residue from one of Dynatech's leach experiments on Meridian lignite. In addition to the petrographic analysis, we performed an ash determination to help establish the dissolution level of the ash, as well as the organic coal components. The ash level in the residue was not substantially different from the average value of the original lignite. This suggests that the ash is not being substantially concentrated in the residue.

This report completes the work that REI agreed to do on this phase of the study. If Dynatech is commissioned by Meridian to perform some of the additional work that Mr. Gleason mentioned while he was here, I am sure that we can assist you again in characterization of feeds and residues and in the interpretation of results.

Please call and let me know how the visit went from your end. If other questions should arise, if you wish to have us pursue additional work, or if we can help with a proposal effort to continue the work, we will be happy to cooperate.

Very truly yours,

William J. Mallio

Dr. William J. Mallio
Vice President

WJM/rmm

Attachments (3)

Sept. 13, 1982

PETROGRAPHIC COMPARISON OF LIGNITE AND LEACHED RESIDUE

The following descriptions refer to photomicrographs presented in Figure 1.

R455

R455 is the original lignite sample from which the solid residues were leached. This coal consists of several components or macerals which have been measured quantitatively (by volume %) and are presented in the enclosed petrographic analysis (Table I). It should be noted that this sample has a total vitrinite content of 63.21% and an average vitrinite reflectance in oil of 0.32. The ash was found to be 12.96 (weight%) on a dry basis. This sample exhibits a noticeable banding in its microstructure.

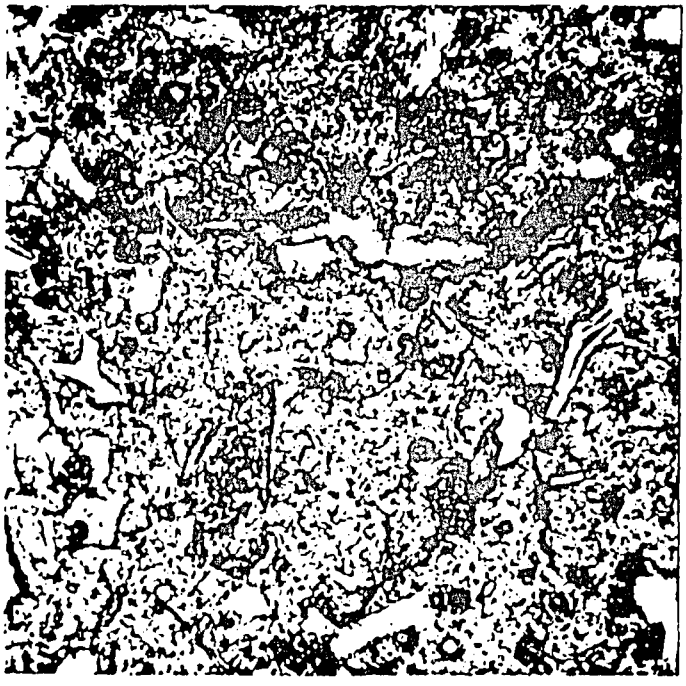
R486 is the solid residue taken from Dynatech's experiment; a high temperature basic leach of the original lignite sample. Remnants of identifiable coal macerals are still present in the residue, however, in much reduced amounts. Total vitrinite is only 6.24% as compared to 63.21% in the original lignite (See Table I). Exinite and semi-fusinite totals also dropped significantly in the residue. These data are based on a quantitative petrographic analysis of the residue. A "residual matrix" was found to be present in the residue which accounted for 64.38% of the total sample (by volume). The matrix is organic and is somewhat similar to coal in its general appearance. However, it is lighter in color than the vitrinite in the original lignite and its reflectance is considerably higher (0.45). The reflectance of the remnant vitrinite particles in the residue was found to be the same as that of the vitrinite in the original lignite. There is a little difference in ash between the two samples. The residue has an ash of 16.36% (dry basis) compared to 12.96% for the lignite. Banding, which was present in the original sample, is noticeably absent in the residue.

R455- Original Lignite Sample

|----------|
0 40μ

R455- Original Lignite Sample

|----------|
0 40μ



R486- Residual Lignite Sample

|----------|
0 40μ

Figure 1

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TABLE I

Sample	V_2	V_3	V	Matrix	VT*	E	R	SF	Total	SF	M	F	MM	Total	Avg Ro
R455 Lignite	15.97	39.11	--		8.13	7.77	0.74	2.40	74.12	4.80	8.50	5.00	7.58	25.88	.32
R486 Residue	--	--	6.24**	64.38		1.62	--	2.17***	--	--	11.65	4.24	9.70	--	.45

Abbreviations for entities:

V_2 = vitrinoid type 2 (average reflectance in oil 0.20 to 0.29, etc.)
E = exinoids
R = resinoids
SF = semi-fusinoids
M = micrinoids
F = fusinoids
MM = mineral matter calculated from following formula:

$$MM = \frac{\dfrac{1.08\ \text{Ash, \%} + 0.55\ \text{Sulfur, \%}}{2.8\ (\text{avg. sp. gr. of mineral matter})}}{\dfrac{100 - (1.08\ \text{Ash, \%} + 0.55\ \text{Sulfur, \%})}{1.35\ (\text{avg. sp. gr. of coal entities})} + \dfrac{1.08\ \text{Ash, \%} + 0.55\ \text{Sulfur, \%}}{2.8}} \times 100$$

*VT = telinite or cellular vitrinite
**Includes all vitrinoid types
***Includes all semi-fusinoid types

Resource Engineering Incorporated

80 Bacon Street, Waltham, Massachusetts 02154 (617) 894-6720

DATE September 9, 1983

ULTIMATE AND PROXIMATE ANALYSIS

YOUR PURCHASE ORDER # 29674 ANALYSIS REPORT: A 895

SAMPLE RECEIVED: 8/18/83 SAMPLE: Lignite Residue

RECEIVED FROM: Dynatech R/D Co.
99 Erie Street
Cambridge, MA 02139

Attn: Dr. Debra Trantolo

	AS RECEIVED	DRY BASIS
% MOISTURE	6.54	---
% ASH	20.30	21.72
% VOLATILE MATTER	36.30	38.84
% FIXED CARBON	36.86	39.44
% SULFUR	0.27	0.29
% CHLORINE	0.02	0.02
% CARBON	51.43	55.03
% HYDROGEN	3.11	3.33
% NITROGEN	.58	.62
% OXYGEN (By Difference)	17.75	18.99
BTU/LB.	8518	9115
MAF - BTU/LB.	---	11643

RESPECTFULLY SUBMITTED BY Thomas E. Schuler

Thomas Schuler
Laboratory Manager

Resource Engineering Incorporated

80 Bacon Street, Waltham, Massachusetts 02154 (617) 894-6720

TO: Dr. Debra Trantolo
Dynatech R/D Co.
99 Erie Street
Cambridge, MA 02139

FROM: John R. Pilling
Resource Engineering Inc.

DATE: September 9, 1983

SUBJECT: Petrographic Analysis of Leached Residue

The following description refers to photomicrographs presented in Figure 1.

A 895 A895 is the solid residue taken from Dynatech's experiment; a high temperature basic leach of the original lignite sample. Remnants of identifiable coal macerals are still present in the residue; however, in much reduced amounts. Total vitrinite is only 12.1% as compared to 64.8% in the lignite received 4/27/83 (See Table 1). Exinite, semi-fusinite and fusinite totals also dropped significantly in the residue. These data are based on a quantitative petrographic analysis of the residue. A "residual matrix" was found to be present which accounted for 62.8% of the total residue sample (by volume). The matrix is organic and is somewhat similar to coal in its general appearance. However, it is lighter in color than the vitrinite in the original lignite and its reflectance is considerably higher (0.63) as compared to the lignite (0.31). The reflectance of the remnant vitrinite particles in the residue (0.30) was found to be the same as that of the vitrinite in the original lignite (0.31). There is considerable difference in ash between the two samples. The residue has an ash of 21.72% (dry basis) compared to 7.73% for the lignite. Banding, which was present in the original lignite, is noticeably absent in the residue. The ultimate analyses of the two materials show some differences in the carbon, hydrogen and nitrogen values on a dry basis (See Table 2). The residue has a carbon of 55.03% as compared to 68.60% in the original lignite. Hydrogen for the residue is 3.33% as compared to 4.07% for the lignite, and nitrogen is 0.62% for the residue as compared to 0.84% for the lignite.

John R. Pilling, Geologist

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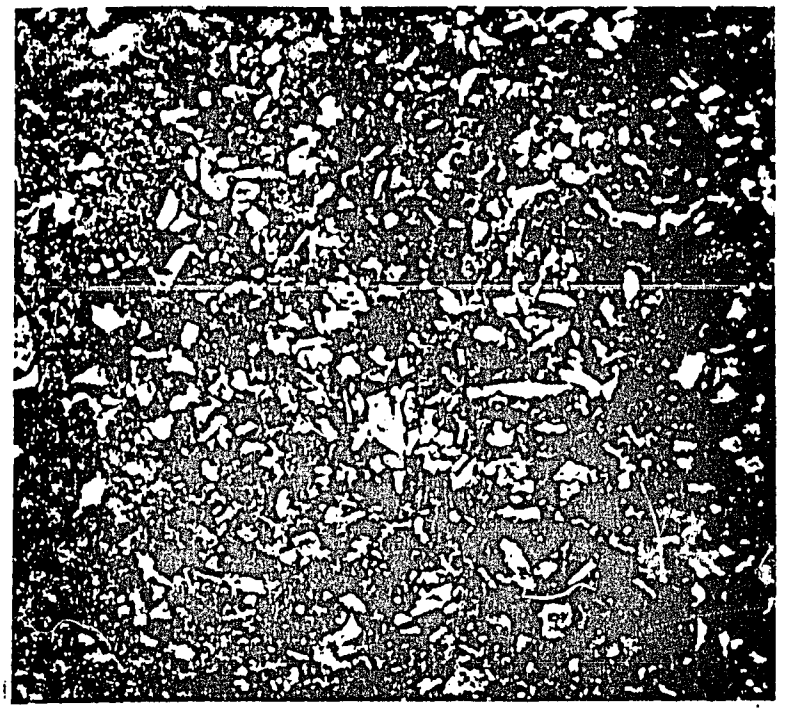
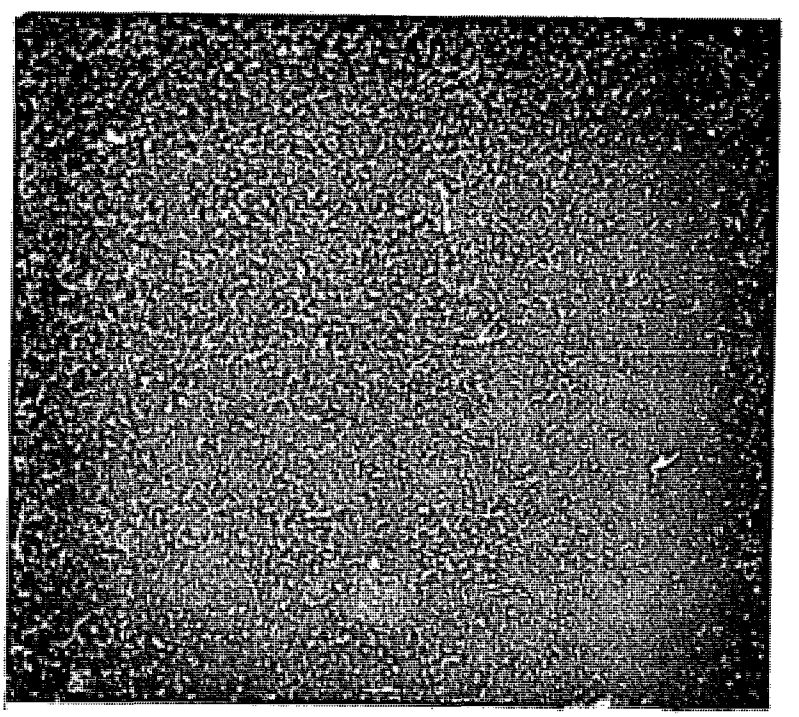


A 895 Residue from leaching lignite sample showing remnants of original lignite particles embedded in "residual matrix".

|----------|
0 40μ



A 895 Common texture of "residual matrix" in residue. The residual matrix accounts for more than 60% of the volume of the residue.

|----------|
0 40μ

Figure 1

Resource Engineering Incorporated

80 Bacon Street, Waltham, Massachusetts 02154 (617) 894-6720

July 5, 1983

Dr. Debra Trantolo
Dynatech R/D Co.
99 Erie Street
Cambridge, MA 02139

Dear Debra,

Attached is our report on the original coal (Buelah lignite) and the residue after leaching. The data suggests that the vitrinite component has been affected and the volume replaced by the "residual matrix". Note that the microstructure and reflectance of the "matrix" is very different from that of vitrinite. The overall chemical composition must not be substantially different, however, as indicated by the comparison of the ultimate analysis of the residue as compared to that of the starting material.

This suggests two possibilities: (1) the residual matrix may be a precipitate upon removal from the system; and (2) the residual matrix may be a reaction intermediate. That is, the "matrix" may be in an altered state, where the lignite structure has been partly broken down, changing it's physical appearance.

I suggested, when we met last week, that an infrared scan be made of the starting material and the residue. This might give some hint, in a broad way, of changes in bonding.

Please let me know if anything else is needed.

Very truly yours,

Bill Mallio

Dr. W. J. Mallio
Vice President

WJM/vs
Enc.

Resource Engineering Incorporated

80 Bacon Street, Waltham, Massachusetts 02154 (617) 894-6720

DATE June 7, 1983

COAL ANALYSIS REPORT

ULTIMATE AND PROXIMATE ANALYSIS

YOUR PURCHASE ORDER # 29166 ANALYSIS REPORT: A 790

SAMPLE RECEIVED: 4/27/83 SAMPLE: Lignite Buelah Zap

RECEIVED FROM: Dr. Debra Trantola

Dynatech R/D Company
99 Erie Street
Cambridge, MA 02139

	AS RECEIVED	DRY BASIS
% MOISTURE	38.25	
% ASH	4.77	7.73
% VOLATILE MATTER	26.24	42.49
% FIXED CARBON	30.74	49.78
% SULFUR	0.34	0.55
% CHLORINE	0.03	0.05
% CARBON	42.36	68.60
% HYDROGEN *	2.51	4.07
% NITROGEN	0.52	0.84
% OXYGEN * (By Difference)	11.21	18.16
BTU/Lb	6986	11313
MAF - BTU/Lb.	-	12260

* Excluding moisture

cc: Dr. Donald L. Wise

RESPECTFULLY SUBMITTED BY Thomas Schuler
Thomas Schuler
Laboratory Manager

Resource Engineering Incorporated

80 Bacon Street, Waltham, Massachusetts 02154 (617) 894-6720

DATE June 7, 1983

COAL ANALYSIS REPORT

YOUR PURCHASE ORDER # 29166 ANALYSIS REPORT: A 790

SAMPLE RECEIVED: 4/27/83 SAMPLE: Lignite Buelah Zap

RECEIVED FROM: Dr. Debra Trantola

Dynatech R/D Company
99 Erie Street
Cambridge, MA 02139

ASH ANALYSIS

% SiO_2	20.5
% Al_2O_3	11.3
% Fe_2O_3	3.22
% CaO	28.0
% MgO	8.55
% Na_2O	3.05
% K_2O	0.53
% TiO_2	0.63
% MnO	0.16
% P_2O_5	1.08
% SO_3	20.2

RESPECTFULLY SUBMITTED BY Thomas Schuler
Thomas Schuler
Laboratory Manager

cc: Dr. Donald L. Wise

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Resource Engineering Incorporated

80 Bacon Street, Waltham, Massachusetts 02154 (617) 894-6720

TABLE II

DATE June 22, 1983

COAL ANALYSIS REPORT

ULTIMATE AND PROXIMATE ANALYSIS

YOUR PURCHASE ORDER # 29166

ANALYSIS REPORT: A 817

SAMPLE RECEIVED: 6/7/83

SAMPLE: Residual lignite Solids
Post Cook B 017470-1

RECEIVED FROM:

Dr. Debra Trantola
Dynatech R/D Co.
99 Erie Street
Cambridge, MA 02139

	AS RECEIVED	DRY BASIS
% MOISTURE	3.64	
% ASH	13.11	13.61
% VOLATILE MATTER	-	-
% FIXED CARBON	-	-
% SULFUR	0.16	0.16
% CHLORINE	0.03	0.03
% CARBON	63.94	66.36
% HYDROGEN *	3.59	3.73
% NITROGEN	0.88	0.91
% OXYGEN (By Difference)*	14.65	15.20
BTU/Lb.	-	-
MAF - BTU/Lb.	-	-

* Excluding moisture

RESPECTFULLY SUBMITTED BY Thomas Schuler
Thomas Schuler
Laboratory Manager

cc: Dr. Donald L. Wise ✓

Resource Engineering Incorporated

80 Bacon Street, Waltham, Massachusetts 02154 (617) 894-6720

TO: Dr. Debra Trantolo
Dynatech R/D Co.
99 Erie Street
Cambridge, MA 02139

FROM: John R. Pilling
Resource Engineering, Inc.
80 Bacon Street
Waltham, MA 02154

DATE: July 5, 1983

SUBJECT: Petrographic Comparison of Lignite and Leached Residue

The following descriptions refer to photomicrographs presented in Figure 1.

A790

A790 is the original lignite sample from which the solid components or macerals which have been measured quantitatively (by volume %) and are presented in the enclosed petrographic analysis (Table 1). It should be noted that this sample has a total vitrinite content of 64.8% and an average vitrinite reflectance in oil of 0.31. The ash was found to be 7.73 (weight %) on a dry basis. This sample exhibits a noticeable banding in its microstructure.

A817

A817 is the solid residue taken from Dynatech's experiment; a high temperature basic leach of the original lignite sample. Remnants of ider coal macerals are still present in the residue; however, in much reduced a Total vitrinite is only 16.2% as compared to 64.8% in the original lignite (S 1). Exinite, semi-fusinite and fusinite totals also dropped significantly esidue. These data are based on a quantitative petrographic analysis of the . A "residual matrix" was found to be present in the residue which accounted for 64.3% of the total sample (by volume). The matrix is organic and is somewhat similar to coal

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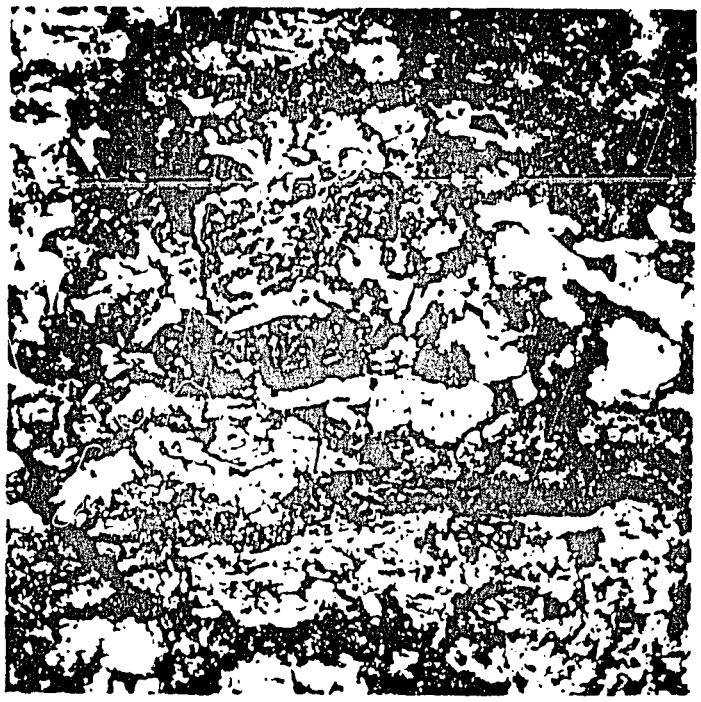
in its general appearance. However, it is lighter in color than the vitrinite in the original lignite and its reflectance is considerably higher (0.71). The reflectance of the remnant vitrinite particles in the residue was found to be the same as that of the vitrinite in the original lignite. There is some difference in ash between the two samples. The residue has an ash of 13.61% (dry basis) compared to 7.73% for the lignite. Banding, which was present in the original sample, is noticeably absent in the residue. The ultimate analyses of the two materials show some noticeable similarities in the carbon, hydrogen and nitrogen values on a dry basis (See Table 2). The residue has a carbon of 66.36% as compared to 68.60% in the original lignite. Hydrogen for the residue is 3.73% as compared to 4.07% for the lignite, and nitrogen is 0.91% for the residue as compared to 0.84% for the lignite.

John R. Pilling
Geologist

JRP/vs



A790 Original Lignite Sample

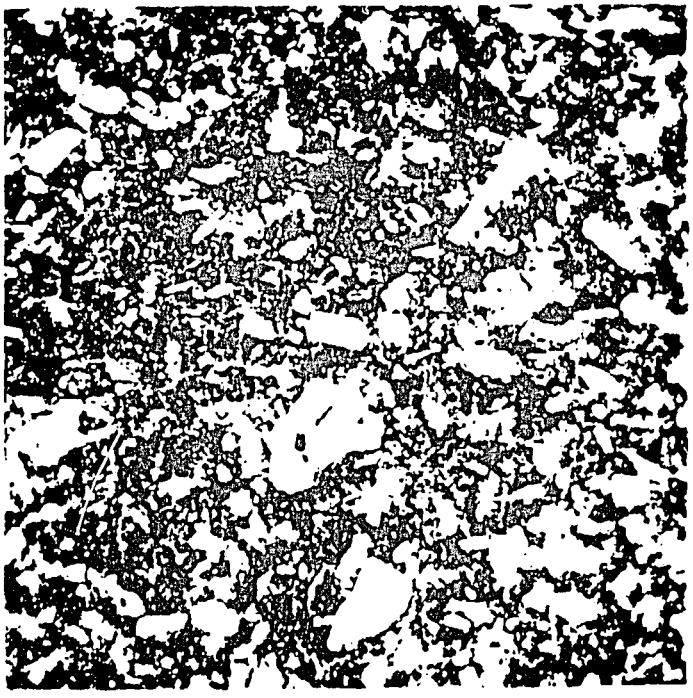
|----------|

0 40μ

A790 Original Lignite Sample

|----------|

0 40μ



A817 Residual Lignite Sample

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0 40μ

Figure 1

TABLE I

Sample	V_2	V_3	V_4	V	V	Matrix	VT*	E	R	SF	Total SF		M	F	MM	Total	Avg. Ro
A 790																	
Lignite	27.50	25.30	2.19				9.85	6.98	1.92	1.02	74.76	2.04	8.22	10.61	4.37	25.24	0.31
A 817																	
Residue	--	--	--	16.15**		64.32		0.65	--	1.01***	--	--	9.41	0.74	7.72	--	0.71

Abbreviations for entities:

V_3 = vitrinoid type 3 (average reflectance in oil 0.30 to 0.39, etc.)

E = exinoids

R = resinoids

SF = semi-fusinoids

M = micrinoids

F = fusinoids

*VT = telinite or cellular vitrinite

MM = mineral matter calculated from following formula:

$$\frac{\dfrac{1.08\ \text{Ash, \%} + 0.55\ \text{Sulfur, \%}}{2.8\ \text{(avg sp gr of mineral matter)}}}{\dfrac{100 - (1.08\ \text{Ash, \%} + 0.55\ \text{Sulfur, \%})}{1.35\ \text{(avg sp gr of coal entities)}} + \dfrac{1.08\ \text{Ash, \%} + 0.55\ \text{Sulfur, \%}}{2.8}} \times 100$$

** Includes all vitrinoid types

*** Includes all semi-fusinoid types

Resource Engineering Incorporated

80 Bacon Street, Waltham, Massachusetts 02154 (617) 894-6720

DATE Nov. 28, 1983

ANALYSIS REPORT

ULTIMATE AND PROXIMATE ANALYSIS

YOUR PURCHASE ORDER # 29942 ANALYSIS REPORT: A 942

SAMPLE RECEIVED: 10/27/83 SAMPLE: Lignite: Beulah Zap

RECEIVED FROM: Dynatech R/D Company
99 Erie Street
Cambridge, MA 02139

Attn: Dr. Debra Trantola

	AS RECEIVED	DRY BASIS
% MOISTURE	34.69	--
% ASH	6.83	10.46
% VOLATILE MATTER	30.13	46.13
% FIXED CARBON	28.35	43.41
% SULFUR	0.74	1.14
% CHLORINE	0.02	0.03
% CARBON	43.05	65.91
% HYDROGEN*	2.70	4.13
% NITROGEN	.55	0.84
% OXYGEN* (By Difference)	11.42	17.49
BTU/Lb.	7059	10808
MAF BTU/Lb.		12070

RESPECTFULLY SUBMITTED BY Thomas L. Schuler
Thomas Schuler
Laboratory Manager

* Excluding Moisture

SAMPLE	V_2	V_3	V	V	V	V	V	V	V	V	VT*	E	R	SF	TOTAL	SF	M	F	MM	TOTAL	AV. RO
A 942 Lignite	28.45	24.23									10.13	7.22	1.41	4.22	75.66	-	8.23	9.84	6.27	24.34	0.28

Abbreviations for entities:

V_3 = vitrinoids
E = exinoids
R = resinoids
SF = semi-fusinoids
M = micrinoids
F = fusinoids
*VT = telinite or cellular vitrinite
MM = mineral matter calculated from following formula:

$$\frac{1.08\ \text{Ash, \%} + 0.55\ \text{Sulfur, \%}}{2.8\ \text{(avg sp gr of mineral matter)}}$$

$$\text{MM} \quad \frac{100 - (1.08\ \text{Ash, \%} + 0.55\ \text{Sulfur, \%})}{1.35\ \text{(avg sp gr of coal entities)}} + \frac{1.08\ \text{Ash, \%} + 0.55\ \text{Sulfur, \%}}{2.8} \times 10$$

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Appendix B

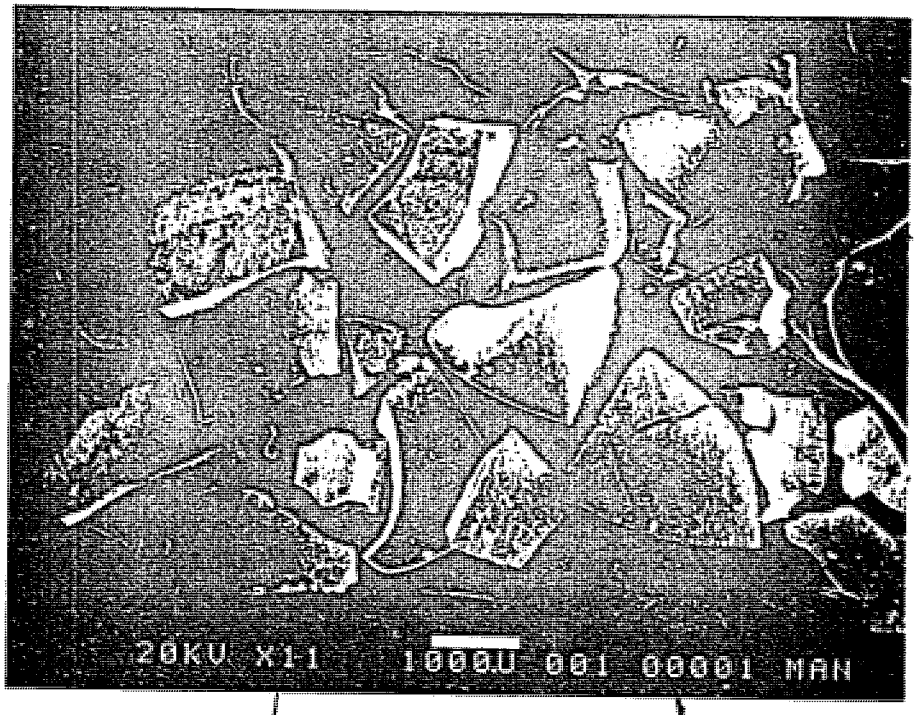
SCANNING ELECTRON MICROGRAPHS

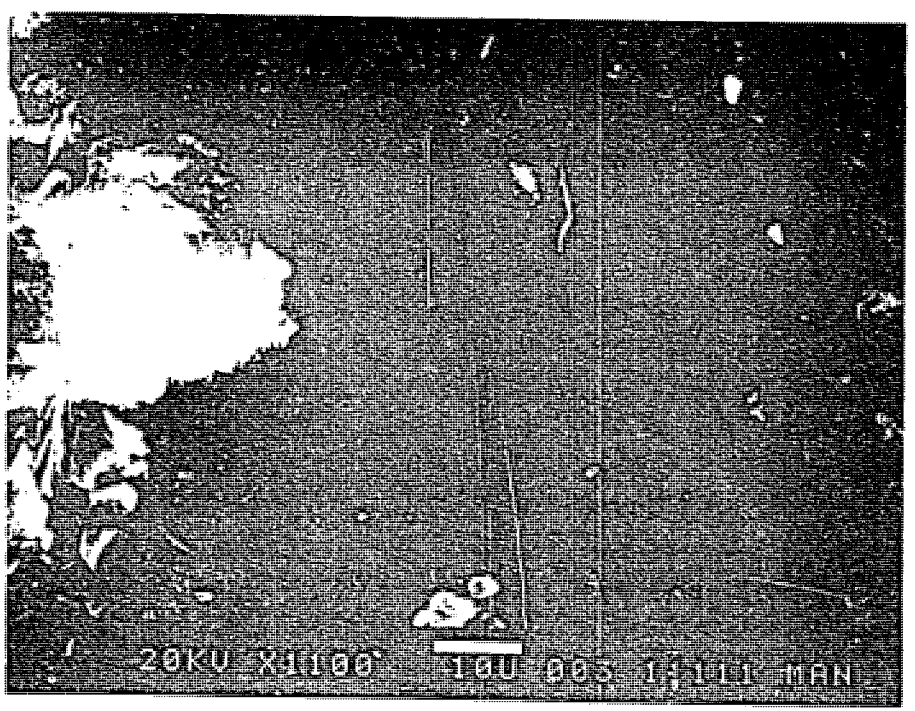
As Submitted By:

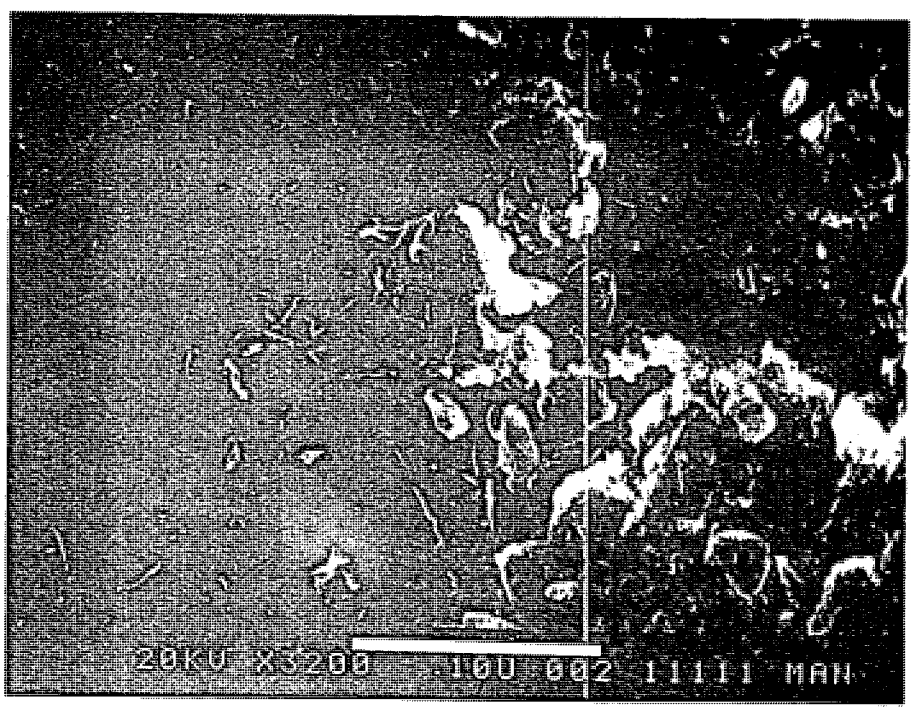
Manlabs, Inc.
Cambridge, MA 02139

These micrographs were done on residues from the "base case" pretreatment of Buelah lignite (8% volatile solids, 20% sodium carbonate). A sample of the original slurry was retained for analysis. Subsequent samples were taken at 150°C, 200°C, and 250°C. Micrographs were recorded at various magnifications and sample surfaces characterized via EDAX (Energy Distribution Analysis via X-ray). EDAX results are detailed in the text.

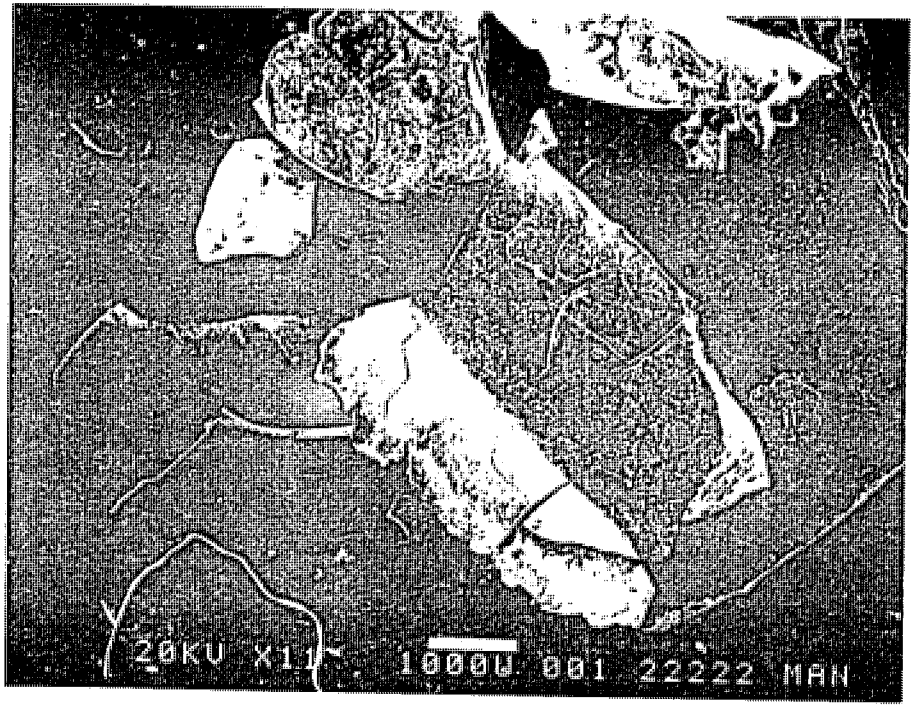
SAMPLE A: ORIGINAL LIGNITE

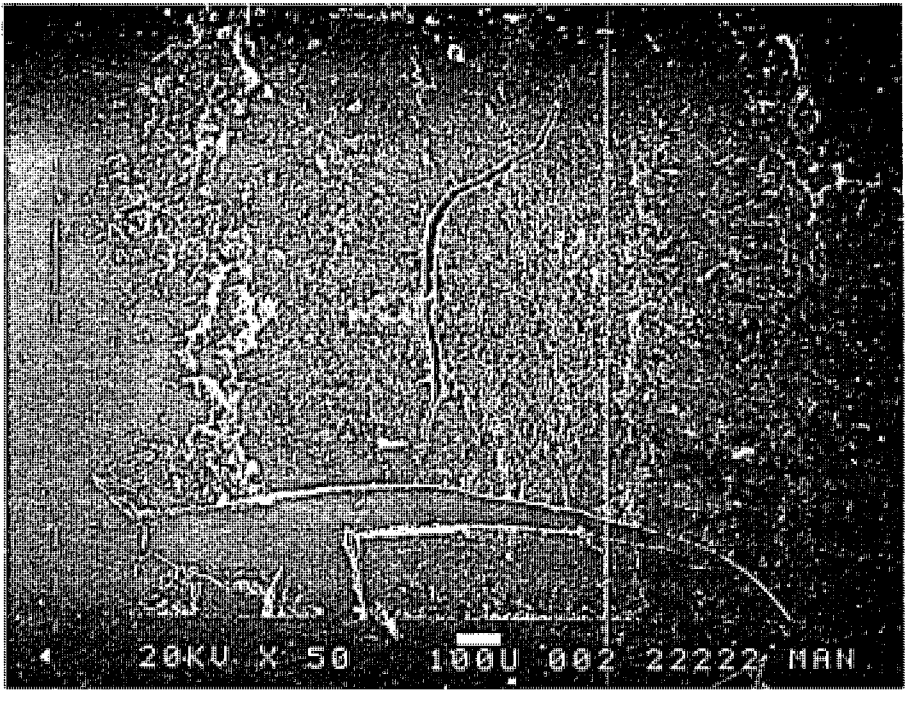






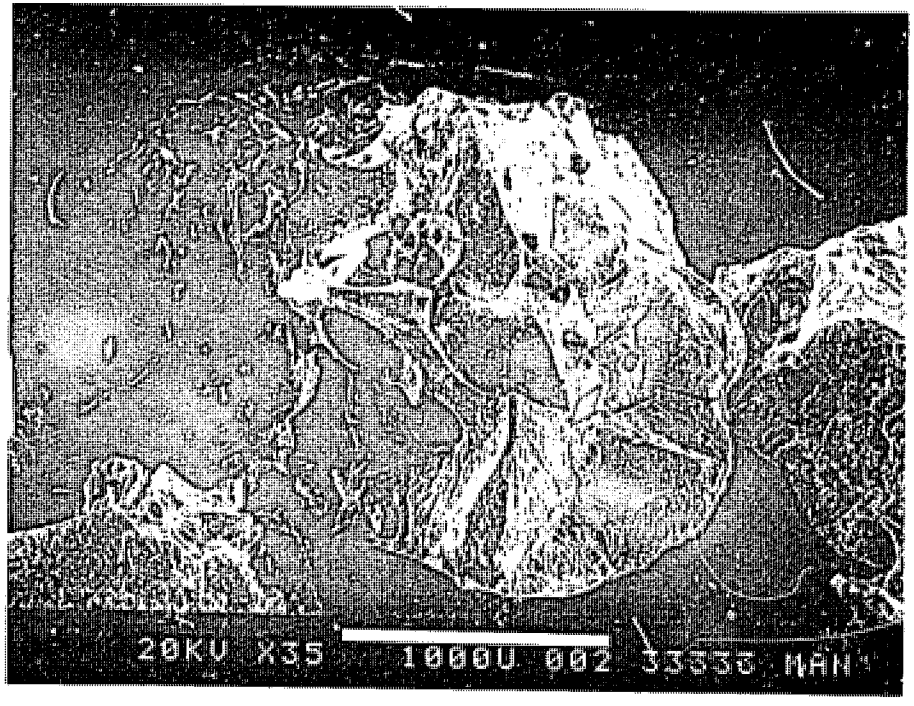
SAMPLE B: 150°C

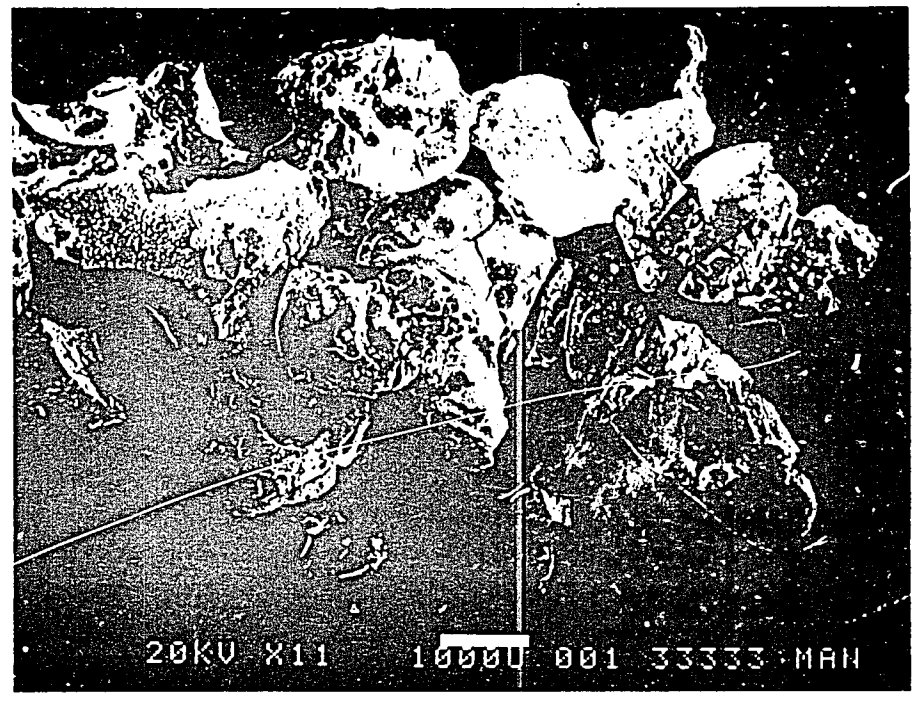




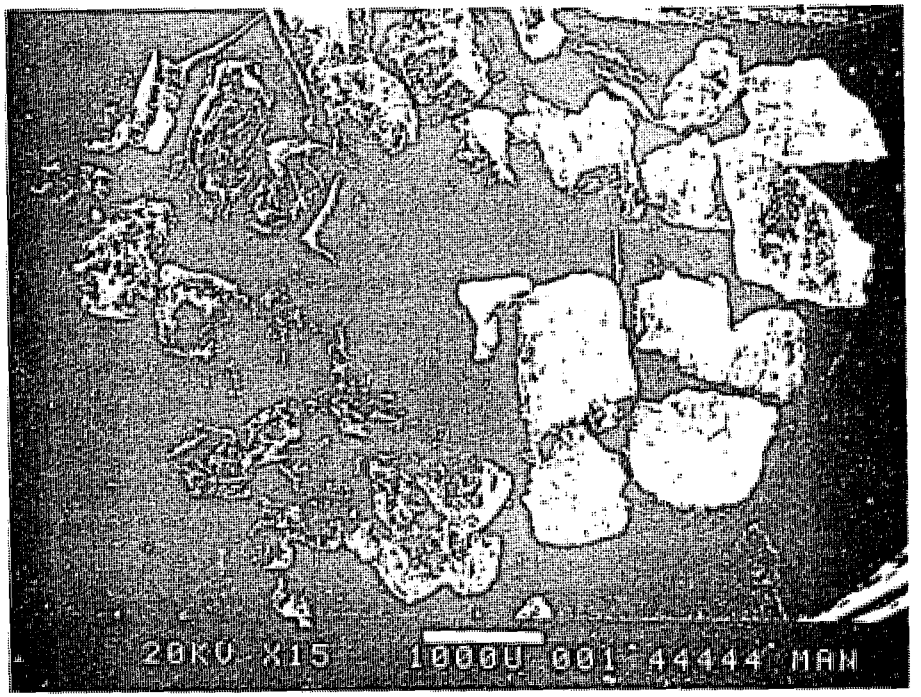
2/2

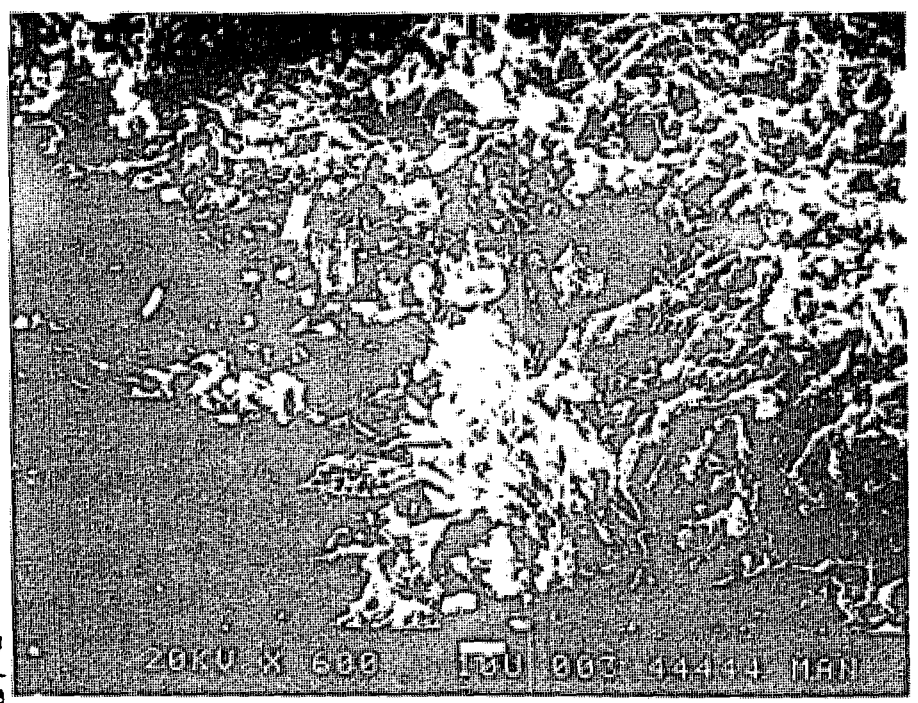
SAMPLE C: 200°C

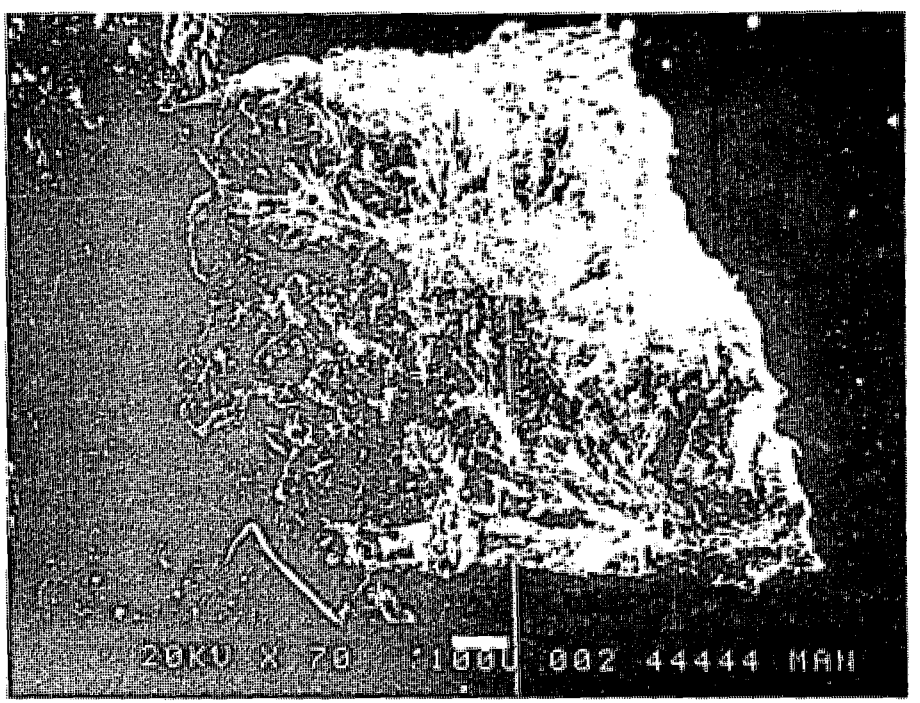




SAMPLE D: 250°C







Appendix C

THE INDUSTRIAL/UNIVERSITY REVIEW COMMITTEE

An Industrial/University Review Committee was organized to review the technical accomplishments of this liquefaction program. The regular review by members of the committee provided continued guidance for project direction. This monitoring by IURC members was intended to insure that technologies that result from this program will be transferred from DoE sponsorship to industrial sponsorship.

Two formal meetings were held with the IURC, one at the program inception and one at its completion. The agendas for these two meetings are enclosed, as well as a complete listing of IURC members. Informal review meetings with IURC members were also included during the course of this program.

INDUSTRIAL/UNIVERSITY REVIEW COMMITTEE

"Direct Liquefaction of Peat and Lignite to BTX-Type Liquid Fuel"

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AGENDA -

INDUSTRIAL/UNIVERSITY REVIEW COMMITTEE MEETING

September 28, 1983

"Direct Liquefaction of Peat and Lignite to BTX-Type Liquid Fuel"

9:00 am	Introduction Debra J. Trantolo, Program Manager
9:15 am	The Project and the Department of Energy Donald L. Wise
9:30 am	The Project and Meridian Land and Minerals David S. Gleason, Committee Chairperson
9:45 am	Coffee and Doughnut Break
10:00 am	The Chemistry D.J. Trantolo
10:15 am	The Process Peter F. Levy
10:30 am	Results to Date D.J. Trantolo
10:45 am	Present Work and Plans D.J. Trantolo
11:00 am	Discussion: Specific Comments and Recommendations D.S. Gleason, Moderator
12:00 noon	Luncheon The Engineer's Club, Prudential Building, Boston
	Closing Remarks D.J. Trantolo D.S. Gleason

GENERAL NOTES FROM IURC MEETING OF SEPTEMBER 28, 1983

- A crucial questions is whether continued work should be at higher temperatures and shorter reaction times. Some experiments should be done to determine if higher yields are obtained from high temperatures and shorter times, or lower temperatures and longer times.

- Should keep in mind that this is an applied research program. The work should be directed at those things that are most important, those with the greatest economic impact. Where do we get the best yield at the economic optimum? What we need first is a model of reasonable options. We need a model to hypothesize a reasonable result -- need to define the program using a process model.

- An initial step might be to form a process design model rather than continued gathering of data.

- Agree with the concern about process concept rather than technical data. Has there been any attempt to look at ways to improve economics in a big hurry? Reviewer believes some confusion on the question of volatile vs. nonvolatile solids; we need a project nomenclature. Reviewer believes this is an ambitious project -- believes we shouldn't overextend what we are trying to do.

- Inserts a note supporting the idea that we have to have some fundamental data (in response to discussion on modeling).

- Stresses again the idea that a conceptual model is important.

- We could spend all the money on the project on modeling -- what is needed is to have lab people who are willing to make optimistic projections.

- There is a possibility that the findings might be better in a nonfuel than in a fuel application.

- Maybe there is more financial reward to be gained by conversion to alternating non-fuel, i.e., chemical lignite products. Expresses concern about what happens to the sodium during the running of the experiment. (Discussion concerning what happens to the sodium during the reaction.)

- Thinks we should look at the commercial angle. Discusses projects in Yugoslavia to derive other kinds of products from lignite.

- Believes it is important to recognize the extended peat work done at Dynatech in both modeling and process development work -- stresses that there has been little work done with lignite in process development aspects -- there may be opportunities to develop processing steps for the future.

- Stresses problems connected with where and when we should develop a model -- problems of time and financing.

- Stresses the importance of the limited time available. Believes we should determine which products have been produced to date. Says we should conduct an analysis of product formed.

- Recommendation to monitor viscosity of solution at various points in the process and to determine what products have been produced.

- What are the solids residue? What is the difference between residues from peat and lignite? (Discussion: fact that peat is easily solubilized with very little residue.)

- In any commercial application must know characteristics of the residues, this must not be ignored. Is this a good fuel or what? Must know if you are going to have a lot of toxic residues to get rid of. Stresses that different source of lignite will give different results.

- Discussed fact that the residue is not that much different from the original lignite. This residue might have potential as a fuel in and of itself. Must keep in mind that the ash levels have been increased.

- Prof. McGinnis discussed a Canadian process for cooking of plant materials. The process involved adding a small amount of active aromatics which appears to stop the polymerization reaction and keep the lignin solubilized. He believes there should be studies done at lower temperatures. Also, need some way to decide quickly during the course of the experiment whether it is a good product or not.

- A viscosity probe might be used. Could be loaded on the stirrer on the reactor.

- Knowing the final composition is crucial. Ultimate composition is important.

Project Review

Direct Liquefaction of Peat and Lignite to BTX-Type Fuel

Thursday, August 9, 1984
Museum of Science, Boston, MA

TIME	PRESENTATION	SPEAKER
08:45 - 09:00	INTRODUCTION	Debra J. Trantolo, Ph.D. Dynatech R/D Company
09:00 - 09:15	OVERVIEW	Donald L. Wise, Ph.D. Dynatech R/D Company
09:15 - 09:45	ACID HYDROLYSIS OF LIGNOCELLULOSIC MATERIALS	Hans Grethlein, Ph.D. Prof. of Chemical Engineering Dartmouth College
09:45 - 10:15	ALKALINE HYDROLYSIS OF LIGNOCELLULOSIC MATERIALS	Gary McGinnis, Ph.D. Forest Products Utilization Laboratory Mississippi State University
10:15 - 10:30	COFFEE BREAK	
10:30 - 11:00	LIQUEFACTION OF LIGNITE TO BTX-TYPE FUEL	Debra J. Trantolo
11:00 - 11:30	PROCESS OVERVIEW-ENGINEERING ASPECTS	Stephen G. Haralampu, Sc.D. Dynatech R/D Company
11:30 - 12:00	A LIGNITE CONVERSION SYSTEM	Ernest E. Kern, Ph.D. Consulting Engineering Houston Lighting and Power Company
12:00 - 01:30	LUNCH (SONESTA HOTEL)	
01:30 - 02:00	USE OF LIGNIN WASTES IN COAL LIQUEFACTION	Robert Coughlin, Ph.D. Prof. of Chemical Engineering University of Connecticut
02:00 - 02:15	CATALYSIS OF LOW GRADE COAL CONVERSION	Kenneth Nicholas, Ph.D. Prof. of Chemistry University of Oklahoma (Summary Presentation by DJT)
02:15 - 02:30	COMMERCIALIZATION OF PEAT DE-CARBOXYLATION	John Rohrer Vice President - Engineering Signal Cleanfuels Inc.
02:30 - 03:00	COMMERCIALIZATION OF THE NOVEL COAL INDUSTRIES	Burl Davis Project Manager Gulf R/D Company
03:00 - 04:00	DISCUSSION AND RECOMMENDATIONS	